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Beckmann Rearrangement in Liquid Sulfur Dioxide[1]. *IV. Syntheses of 1-Methyl-3,4-dihydro-isoquinoline and 9-Phenyl-phenanthridine*

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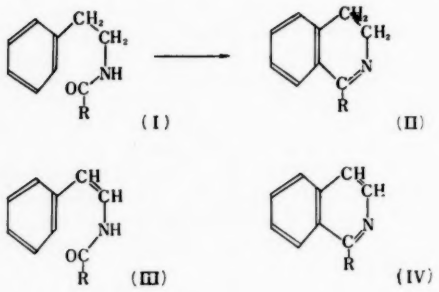
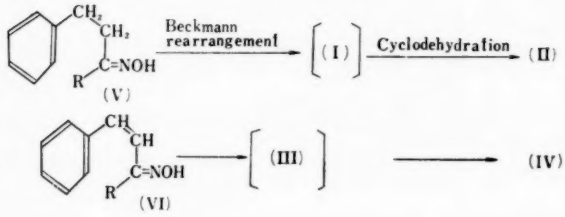
The increasing interest in the syntheses of isoquinoline derivatives which are found in alkaloids extensively has developed three important methods[2] since the beginning of this century. The Bischler-Napieralski reaction consists in the cyclodehydration of *N*-phenethylamides of aliphatic or aromatic carboxylic acids (I) to 1-alkyl- or 1-aryl-3,4-dihydroisoquinolines (II), or of *N*-styrylamides of aliphatic or aromatic carboxylic acids (III) to 1-alkyl- or 1-aryl-isoquinolines (IV), by heating at a high temperature with phosphorus pentoxide:

Chart 1.



The starting materials for such a cyclodehydration, acid amides I or III, may be conveniently derived from oximes V or VI by the Beckmann rearrangement. Though several attempts[3-6] have been made to synthesize isoquinoline derivatives from such oximes without isolating the intermediate acid amides, the synthetic value of such simultaneous methods has still been in doubt[2] and the yields of

Chart 2.



isoquinolines were very scarce except in a few special cases. Only when the benzene rings bore electron donating groups such as alkyl, alkoxyl, etc., the yields of the isoquinolines were promoted[7,8].

In the preceding papers[1], the authors reported that liquid sulfur dioxide was a superior solvent for the Beckmann rearrangement. Generally, the rearrangement in this solvent was accomplished instantaneously at the room temperature giving excellent yields.

In addition, the authors have recently been able to get another piece of information concerning the usefulness of liquid sulfur dioxide. Bradsher and Sinclair[9] employed phosphorus pentoxide in liquid sulfur dioxide at $-10°C$ for cyclodehydration of *o*-benzylacetophenone and its derivatives to obtain anthracene derivatives in good yields.

As a preliminary examination, *N*-phenethylacetamide (I, $R=CH_3$) was subjected to the Bischler-Napieralski reaction with phosphorus pentoxide in liquid sulfur

1) Part III of this series: R. Tada and N. Tokura, This Bulletin, **31**, 387 (1958).
2) Roger Adams, "Org. Reactions", Vol. VI, pp. 74—100, John Wiley and Sons, New York (1951).
3) S. Komatsu, *Mem. Coll. Kyoto Imp. Univ.*, **7**, 147 (1924). *Chem. Abstr.*, **18**, 2126 (1924).
4) C. Goldschmidt, *Ber.*, **27**, 1954, 2795 (1894), ibid., **28**, 818 (1895).
5) C. S. Gibson, K. V. Hariharan, K. N. Menon and J. L. Simonsen, *J. Chem. Soc.*, **1926**, 2247.
6) P. A. S. Smith, *J. Am. Chem. Soc.*, **76**, 436 (1954).
7) K. N. Gaind, S. Kopoar and J. N. Ray, *J. Indian Chem. Soc.*, **18**, 213 (1941).
8) S. Sugasawa, *J. Chem. Soc.*, **1933**, 1583.
9) C. K. Bradsher and E. F. Sinclair, *J. Org. Chem.*, **22**, 79 (1957).

TABLE I

SYNTHESES OF 1-METHYL-3,4-DIHYDROISOQUINOLINE FROM BENZYLACETONE OXIME IN LIQUID SO_2[a, b]

No.	Reagent	Molar ratio of oxime to reagent	Reaction		*N*-Phenethyl acetamide yield (%)	1-Methyl-3,4-dihydroisoquinoline yield (%)
			temp.(°C)	time(hr.)		
1	P_2O_5	1 : 5	20	6	10.0	4.5[c]
2	P_2O_5	1 : 5	20	12	20.0	trace
3	P_2O_5	1 : 5	−10	12	trace	0
4	P_2O_5	1 : 5	70	6	15.0	15.9
5	$P_2O_5+SOCl_2$	1 : 5 : 5	70	6	trace	0
6	$P_2O_5+POCl_3$	1 : 5 : 10	50	12	40.0	13.6
7	$P_2O_5+POCl_3$	1 : 5 : 10	70	3	36.0	18.1
8	$P_2O_5+POCl_3$	1 : 5 : 10	70	6	24.0	40.9
9	$P_2O_5+POCl_3$	1 : 5 : 10	70	12	4.0	45.4[d]
10	$P_2O_5+POCl_3$	1 : 5 : 10	110	12	0.0	29.5
11	$P_2O_5+POCl_3$	1 : 5 : 10	70	12	10.0	13.6[e]
12	$P_2O_5+POCl_3$	1 : 5 : 10	70	12	6.0	18.1[f]

a) Reactions were caused to proceed with 5 g. (0.03 mole) of the oxime in 70 ml. of liq. SO_2.
b) $POCl_3$, $SOCl_2$, PCl_5, or SO_3, used as the reagent in liquid sulfur dioxide (molar ratio of oxime to reagent was 1 : 5) at 20°C for 12 hr. or at 70°C for 6 hr., caused no reaction.
c) Reaction with shaking.
d) No difference was observed between the reaction with shaking and that without shaking.
e) Reaction was caused to proceed without solvent (liquid SO_2).
f) Tetralin (70 ml.) was added to the reaction mixture.

dioxide by modifying Bradsher and Sinclair's cyclodehydration. It was ascertained that 1-methyl-3,4-dihydroisoquinoline was obtained in a yield of over 40 per cent. The results and the related facts observed will be reported elsewhere.

From the facts mentioned above, it appeared reasonable to expect that the reaction of the oximes of phenethyl ketones with acidic reagents in liquid sulfur dioxide may well lead to the production of isoquinoline derivatives.

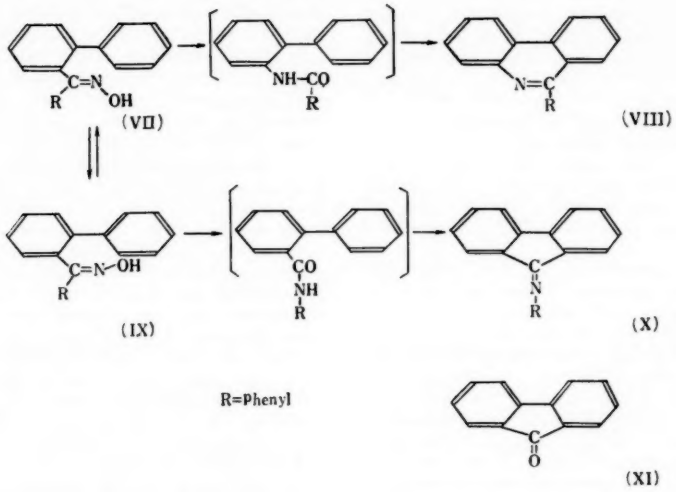
For the purpose of estimating the efficiency of this procedure benzylacetone oxime (V, R=CH_3) seemed suitable and it was subjected to the simultaneous rearrangement and cyclodehydration in liquid sulfur dioxide to obtain 1-methyl-3,4-dihydroisoquinoline (II, R=CH_3). As shown in Table I, the best result (45.4% yield) was attained by treating the oxime with a mixture of phosphorus pentoxide and phosphorus oxychloride at 70°C in liquid sulfur dioxide.

Among various reagents examined, sulfuric acid, sulfur trioxide, thionyl chloride and phosphorus pentachloride were ineffective and phosphorus pentoxide gave a small quantity of the product. But when a mixture of phosphorus pentoxide and phosphorus oxychloride was used at 70°C for twelve hours, the amount of the product reached the maximum (45.4%). As for the reaction temperature, a better yield was obtained at 70°C rather than below 0°C, which differed somewhat from the experience of Bradsher and Sinclair[9]. Shaking of the reaction vessel resulted only in a slight improvement. Addition of another solvent such as tetralin gave no good effect. Because phosphorus pentoxide was not dissolved but suspended in liquid sulfur dioxide, the addition of a large amount of phosphorus oxychloride served probably to keep the suspension homogeneous.

A considerable amount of acid amide (I, R=CH_3) was found in the reaction mixture. This explains the fact that the cyclodehydration is rather a slow reaction and the first step (the Beckmann rearrangement) proceeds promptly before the cyclodehydration takes place. When benzylideneacetone oxime (VI, R=CH_3) was subjected to this reaction, only a resinous product was produced. This suggests that a vinyl polymerisation occurred in liquid sulfur dioxide.

The preparation of 9-phenylphenanthridine (VIII) in liquid sulfur dioxide was attempted. Smith[6] reported that the yield of this substance from *o*-phenylbenzophenone oxime (VII) by heating with polyphosphoric acid was 17 per cent.

Chart 3.



With phosphorus pentoxide and phosphorus oxychloride in liquid sulfur dioxide, 9-phenylphenanthridine (VIII) was obtained in an improved yield of 29.4 per cent. Moreover, fluorenone (XI) was also isolated from the reaction mixture as was reported by Smith.

It is an established fact that a *trans*-migration occurs in the Beckmann rearrangement. When *o*-phenylbenzophenone oxime (VII) takes another geometrical structure IX, it may afford fluorenoneanil (X) as the product. This will produce fluorenone (XI) by hydrolysis in the acidic medium.

The method mentioned above, the simultaneous rearrangement and cyclodehydration in liquid sulfur dioxide under mild conditions, may give excellent syntheses of dihydroisoquinoline, phenanthridine and their derivatives and may be applied extensively with great advantages.

Experimental

Liquid sulfur dioxide.—Commercial sulfur dioxide was dried with sulfuric acid and distilled.

Reagents.—Phosphorus pentoxide, oxychloride, and pentachloride, sulfuric acid, sulfur trioxide and thionyl chloride were of extra pure grade.

Apparatus and general procedure.—Glass pressure vessels (300 ml. capacity) equipped with metal joints and appropriate cocks or valves were used as before[9]. A liquid sulfur dioxide solution of an oxime was added to a mixture or a solution of the dehydrating reagent in the same solvent with ice-cooling. The vessel was kept at a definite temperature during the reaction period for a definite time. If necessary, the vessel was shaken. Then the solvent was evaporated and recovered. The residue was dropped into ice water and the excessive reagent was decomposed. Then the products were separated for their identification.

Synthesis of 1-methyl-3, 4-dihydroisoquinoline from benzylacetone oxime.—*Benzylacetone.*—Essentially the methods of Leuchs[10] and Meerwein[11] were followed. Metallic sodium (42 g.) was dissolved in 500 ml. of absolute ethanol and 500 g. of ethyl acetoacetate was added. To this mixture cooled below 30°C, 246 g. of benzyl chloride was added and the whole was stirred for 1 hour at room temperature. The reaction mixture was further refluxed for 1 hour and filtered. From the filtrate 350 g. of ethyl 2-benzylacetoacetate was obtained as a transparent liquid boiling at 140~145°C (5 mmHg). In an autoclave, a mixture of 350 g. of the ethyl 2-benzylacetoacetate and 200 ml. of water was heated for 30 min. at 250°C. The oily layer and the ethereal extract of the aqueous layer were combined, washed with 50 ml. of 0.1 N sodium hydroxide solution and with water successively, and distilled. Benzylacetone distilled at 105~110°C (10 mmHg). Yield, 160 g.

Benzylacetone oxime.—Prepared by the ordinary method[12], m. p. 84~85°C. From 160 g. of benzylacetone, 134 g. of the oxime was obtained.

1-Methyl-3, 4-dihydroisoquinoline (*II*, $R=CH_3$).—A solution of 5 g. (0.03 mole) of benzylacetone oxime in 20 ml. of liquid sulfur dioxide was added to a mixture of the reagents (molar ratio of oxime, phosphorus pentoxide and phosphorus oxychloride was 1 : 5 : 10) in 50 ml. of the same solvent. After the reaction at 70°C for 12 hours, the solvent (sulfur dioxide) was allowed to

10) H. Leuchs, *Ber.*, **44**, 1510 (1911).
11) H. Meerwein, *Ann.*, **398**, 249 (1913).
12) P. W. Neber and A. Uber, ibid., **467**, 63 (1928).

evaporate from the mixture. The residue was added to ice water and excessive reagents were decomposed. The mixture was extracted with ether. The ethereal solution, after being dried over calcium chloride, was condensed and the residue was distilled in vacuo. The rearranged product, acid amide (I, R=CH_3), was obtained as an oil boiling at 155~157°C (5 mmHg); yield, 0.2 g. (4%). The acid amide was hydrolyzed to phenethylamine with hydrochloric acid, and a picrate of the amine was prepared. The melting point and the mixed melting point with an authentic sample were 167~168°C (reported[13] m. p. 171°C).

The residual aqueous solution was made alkaline with caustic alkali and steam-distilled. The distillate was again made alkaline and extracted with ether. The ether solution, after being dried over magnesium sulfate, was condensed and the residue was distilled in vacuo. A pale yellow oil boiling at 95~105°C (5~6 mmHg) was obtained. This was 1-methyl-3, 4-dihydroisoquinoline. Picrate, yellow needles, m. p. 188~189°C (reported[14] m. p. 188~190°C). No depression of the melting point was observed when mixed with an authentic sample.

Anal. Base: Found; N, 9.74%. Calcd. for $C_{10}H_{11}N$; N, 9.65%. Picrate: Found; N, 15.13%. Calcd. for $C_{16}H_{14}O_7N_4$; N, 14.97%.

Dihydroisoquinoline was not produced with phosphorus oxychloride or with thionyl chloride. Sulfuric acid or sulfur trioxide appeared to produce water soluble substances which could not be separated. The effects of reaction conditions on the yield of 1-methyl-dihydroisoquinoline are listed in Table I.

An attempted synthesis of 1-methyl-isoquinoline from benzylideneacetone oxime (VI, R = CH_3). — Vorländer's[15] recipe was followed. A mixture of 320 g. of acetone, 210 g. of benzaldehyde washed with dilute soda solution, and 200 ml. of water was added to 50 ml. of 10% caustic soda solution in two hours at 10~20°C. The reaction mixture was stirred further for two hours and was allowed to stand for 24 hours at room temperature. The solution was made acidic with hydrochloric acid and the oily layer was separated. The aqueous layer was thoroughly extracted with benzene. The oily layer combined with the benzene extract was washed with water and dried over calcium chloride. After the benzene and the unchanged benzaldehyde were distilled off, a pale yellow oil boiling at 105~110°C (3 mmHg) was obtained. Yield, 180 g. The above benzylideneacetone was mixed with hydroxylamine hydrochloride in methanol. The crystals separated in a few days were recrystallized from 60% ethanol: benzylideneacetone oxime[16], m. p. 114~115°C. Yield, 45 g.

Reaction of benzylideneacetone oxime (VI, R=CH_3).—A solution of 4.8 g. of the oxime in 20 ml. of liquid sulfur dioxide was added to a mixture of reagents (molar ratio of oxime to phosphorus pentoxide and phosphorus oxychloride was 1 : 5 : 10) in 50 ml. of liquid sulfur dioxide. The reaction mixture was treated as described above after 3 hours shaking at 70°C, or 6 hours shaking at room temperature. No significant amount of basic materials was found in the reaction mixture except resinous matters.

Synthesis of 9-phenylphenanthridine (VIII) from *o*-phenylbenzophenone oxime (VII).—*o-phenylbenzophenone.*—This was prepared from fluorene as follows: fluorenone obtained from the oxidation of fluorene[17] was cloven to *o*-phenylbenzoic acid[18] by alkali fusion. *o*-phenylbenzonitrile was prepared from this acid via its acid amide and was treated with phenylmagnesium bromide by Schlenk and Bergmann's[19] method to yield *o*-phenylbenzophenone. From 200 g. of fluorene, 25 g. of the ketone was obtained.

o-Phenylbenzophenone oxime (VII).—This was Prepared by the procedure of Smith[6]. Yield 18.3 g. from 25 g. of the ketone.

9-Phenylphenanthridine (VIII).—A solution of 5.4 g. (0.02 mole) of the oxime (VII) in 20 ml. of liquid sulfur dioxide was added to a mixture of the reagents (mole ratio of oxime: phosphorus pentoxide : phosphorus oxychloride, 1 : 5 : 10) in 50 ml. of liquid sulfur dioxide. After being allowed to stand at 70°C for 3 hours the reaction mixture was treated as described above. The resulting aqueous acidic mixture was made alkaline with ammonia and extracted with benzene. The extract was washed first with dilute, then with conc. hydrochloric acid, and finally with water. Neutralization of the acidic solution precipitated a basic material, which was recrystallized from ethanol to give crystalline 9-phenylphenanthridine. Yield, 1.5 g. (29.4%), m. p. 103~104°C. Picrate: yellow needles, m. p. 247~247.5°C (decomp.) (reported[20] m. p. 242°C (decomp.)). The mixed melting points of the base and of the picrate with the authentic samples respectively showed no depression.

Anal. Base: Found; N, 5.68%. Calcd. for $C_{19}H_{13}N$; N, 5.49%. Picrate: Found; N, 11.94%. Calcd. for $C_{25}H_{16}O_7N_4$; N, 11.57%.

When the benzene solution was condensed, 2.7 g. of dark yellow crystals was obtained. Recrystallization from ligroin (b. p. 60~80°C) gave 2.4 g. of pale yellow plates, m. p. 83~84°C, which showed no depression of the melting point on mixing with fluorenone (m. p. 83~84°C).

When the reaction was conducted at 20°C for 12 hours, 0.2 g. (3.9%) of VIII and 1 g. of XI were obtained. A viscous orange liquid (4.2 g.) was also obtained along with XI from the benzene extracts in this case, the liquid being separated by fractional distillation under a reduced pressure. The liquid which distilled at 190~200°C (1~2 mmHg) contained nitrogen (N, 5.96%), but

13) H. Decker and W. Kropp, *Ber.*, **42**, 2078 (1909).
14) E. Späth, F. Berger and W. Kuntara, ibid., **63**, 137 (1930).
15) D. Vorländer, *Ann.*, **294**, 275 (1897).
16) C. Harries and A. S. de Osa. *Ber.*, **36**, 2998 (1903).
17) J. Schmidt and H. Wagner, ibid., **43**, 1797 (1910).
18) C. Graebe and A. Sc. Rateanu, *Ann.*, **279**, 259 (1894).
19) W. Schlenk and E. Bergmann, ibid., **464**, 34 (1928).
20) A. Pictet and A. Hubert, *Ber.*, **29**, 1188 (1896).

showed no change on refluxing with hydrochloric acid in ethanol.

The authors are indebted to Dr. C. K. Bradsher for his valuable suggestions. The financial support of this project was granted by the Ministry of Education. Liquid sulfur dioxide was donated by the Befu Chemical Industries Co., Ltd., A large quantity of fluorene was kindly given by Dr. T. Yoshida, Yawata Chemical Industries Co., Ltd. The authors are grateful to all.

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Rapid Separation of Radioactive Strontium by Solvent Extraction with TTA-Hexone

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It is an important problem at present to develop a rapid method of separating and estimating radioactive strontium (^{89}Sr, and ^{90}Sr) contained in mixed fission products. Such a method is indispensable for devising a workable procedure for the chemical elimination of strontium from reactor wastes. Previously the authors attempted to separate the fission products into groups by solvent extraction, with TTA (*o*-thenoyl trifluoroacetone)-benzene[1], and cupferron-chloroform[2]. As a result of the experiment, it was found that by the solvent extraction with TTA-benzene at pH 6, and with cupferron-chloroform at pH 4, strontium, cesium, and ruthenium remained in the aqueous phase and the other fission products entered the organic phase. Hence the next problem to be solved is to recover the strontium retained by the aqueous phase after the extraction. The present paper describes an investigation on the separation of strontium from other fission products by liquid-liquid extraction.

TTA (*o*-thenoyl trifluoroacetone), dissolved in benzene, toluene, or xylene, is widely employed as a reagent for solvent extraction of zirconium and cerium from their acidic solutions[3], but there are few papers which treat of the separation from a solution of a given pH value. Khym, Tompkins and Cohen[4] have reported separation of ^{45}Ca, which was produced by Sc(*d*, 2*p*) reaction, by solvent extraction with 0.5 M TTA-benzene from a solution of pH 9. As it seems advantageous to use a reagent-solvent phase of low concentration when the extraction is made, the present authors employed 0.05 M TTA-benzene for the purpose to examine the behavior of strontium. Belonging to the same family with calcium, strontium could not be extracted by the reagent-solvent phase though experiments were conducted over a wide range of pH of the aqueous solution. Afterward, various solvents other than benzene were tried and hexone (methyl isobutylketone) was found to be the best, both because of the high solubility of TTA in it and because of its superior power to effect the separation of strontium. In the following experiments 0.05 M TTA-hexone is always used as the extracting agent for the separation of strontium.

Experimental

Reagents, Materials and Apparatus.—*TTA (o-thenoyl trifluoroacetone)* imported from L. Light & Co. Ltd., England, was dissolved in hexone of extra pure grade to a concentration of 0.05 M. TTA-benzene was prepared by dissolving the reagent in thiophene-free benzene to a concentration of 0.05 M and 0.5 M.

1) T. Kiba, S. Ohashi and K. Yoshizawa, Unpublished paper, read at the 10th Annual Meeting of the Chemical Society of Japan (April, 1957).
2) T. Kiba and M. Kanetani, This Bulletin, **31**, 1013 (1958).
3) G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry", John Wiley & Sons, Inc. New York (1957).
4) J. X. Kyhm, P. C. Tompkins and W. E. Cohen, USAEC, **MDDC-1214** (1947).

Radioactive Strontium.—$^{90}Sr(^{90}Y)$ was imported from Oak Ridge National Laboratory, U.S.A. as nitrate in nitric acid solution, a part of which was diluted to 0.02 N nitric acid solution having an activity of about 10,000 cpm. per 0.2 ml. The mixed fission products (Batch No. 35), ^{45}Ca, and ^{106}Ru were imported from the Oak Ridge National Laboratory and used for the comparative investigation of the method.

Buffer Solution.—A system composed of 0.5 M acetic acid, ammonium acetate and aqueous ammonia was used, and its pH was measured by a glass-electrode pH-meter, Horiba Instrument Co., Japan.

Measurement of Radioactivity.—The radioactivity was measured as β-counting by a G-M counting set (No. 131 G-M tube, mica-window: 2.8 mg./cm^2, counting efficiency for $^{90}Sr(^{90}Y)$: 11.7%, "100" scalor, Kobe Kogyo Co. Ltd.).

Separatory Funnel.—The separatory funnel is a spindle-shaped vessel made of hard glass, with a capacity of 30 ml. In order to prevent the mixing of the two phases when being drained, a type with a small bore above the cock and a large bore below was chosen.

Shaking Machine.—Shaking of the content of the separatory funnel was done by means of an electric vertical oscillator performable 230 double strokes per minute. The equipment can handle six funnels at the same time.

Other chemicals were all of pure grade, and the utensils were of ordinary laboratory types.

Procedure.—In a 30 ml. separatory funnel, place 0.2 ml. of the solution of the mixed fission products or the radioactive nuclides, and add the buffer solution of a definite pH to make 6 ml. Then pour 2 ml. of the organic solvent into the vessel, and stopper tightly. Shake the vessel for five minutes with the electric vertical oscillator. After the phases have disengaged, take out the aqueous layer into a second funnel. Re-extract the aqueous phase in the second funnel with 2 ml. of the organic solvent for five minutes. To the organic phase retained in the first funnel, add 5 ml. of the buffer solution and shake for another five minutes. Combine the aqueous phases of the first and the second funnel in a vessel, and the organic phases in another, and evaporate the content in a porcelain counting dish, and measure the radioactivity with the G-M counting set. Plot the decay curve of the activity or draw a Harley plot to identify the nuclide contained in the sample.

1) The experiments were carried out with 0.5 M TTA-benzene, 0.05 M TTA-benzene, and 0.05 M TTA-hexone at different pH of the solution to determine the optimum pH for the separation of strontium.

2) Some experiments with TTA-hexone were carried out with the buffer solution of the optimum pH for the separation of strontium, containing a known amount of barium nitrate, magnesium nitrate, or calcium nitrate, in order to examine the effect of salts present in the solution on the extraction of strontium.

3) The behavior of calcium in the solution was examined using ^{45}Ca as tracer, and was compared in detail with the behavior of strontium.

4) The effect of such agents as EDTA (disodium ethylenediaminetetra-acetate) and ammonium citrate as masking agent on the extraction was examined.

5) For the purpose of rapidly isolating the radioactive strontium from the aged fission products, a two-step extraction was attempted: a solution of the gross fission products was first treated with 0.05 M TTA-benzene at pH 7, and after the organic layer was discarded, the remaining aqueous phase was shaken with 0.05 M TTA-hexone at pH 8. The radioactivity was measured in each case. The radioactive strontium, ^{89}Sr and ^{90}Sr, came out in the last organic phase.

Results and Discussion

The percentage of the material recovered by extraction from the solution of the fission products of different pH by 0.05 M TTA-benzene and 0.05 M TTA-hexone is shown in Fig. 1. The percentage extraction was computed as the ratio between the counting rate of the organic phase to that of the original solution. Before the counting, the organic phase was, of course, evaporated and dried in a counting sample pan, and the original activity taken in the solution was determined for 0.2 ml. of the stock solution of the fission products.

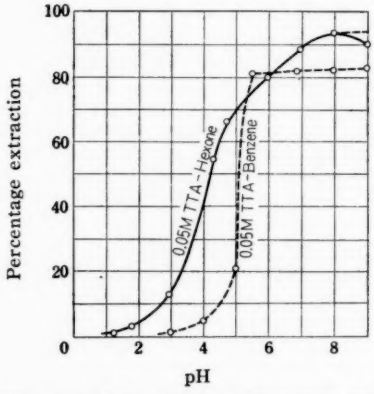

Fig. 1. Effect of pH on the extraction of gross fission products by TTA-benzene and TTA-hexone.

Comparing the results obtained by the extraction with TTA-benzene and TTA-hexone with each other, the amount extracted at pH 8 is greater by the latter than by the former. Since it has been confirmed[1] that after extraction with TTA-benzene at pH 6, strontium, cesium

TABLE I

EXTRACTION OF $^{90}Sr(^{90}Y)$ BY 0.05 M TTA-HEXONE

pH of the solution pH	$^{90}Sr(^{90}Y)$ taken cpm.	Extracted in org. phase cpm.	Retained in aqueous phase cpm.	Extracted %
7	10,050	7,610	2,400	75.8
8	9,220	9,190	30	99.6
9	9,220	9,125	96	98.9

TABLE II

EXTRACTION OF $^{90}Sr(^{90}Y)$ WITH VARIOUS SOLVENTS AT pH 8

Reagent-solvent	$^{90}Sr(^{90}Y)$ taken cpm.	Separation into the phases cpm. (%)	Note: Nuclide and its radiochemical purity
0.5 M TTA-Benzene	8,020	Org. Phase 4,490 (56.0%)	$^{90}Y+^{90}Sr$
		Aq. Phase 3,530	^{90}Sr
0.05 M TTA-Benzene	7,750	Org. Phase 4,290 (55.3%)	^{90}Y (98%)
		Aq. Phase 3,460	^{90}Sr (98~100%)
0.05 M TTA-Hexone	7,540	Org. Phase 7,510	$^{90}Sr+^{90}Y$
		Aq. Phase 30	None

and ruthenium remain in the aqueous phase, the increase in counting rate of TTA-hexone phase should perhaps be attributed to strontium. The following experiment will confirm this supposition.

A solution containing $^{90}Sr(^{90}Y)$ was adjusted to a different pH, and the extraction was carried out with 0.05 M TTA-hexone. The partition of the radioactivity between the aqueous phase and the organic phase was determined as the ratio of their counting rates. As shown in Table I the $^{90}Sr(^{90}Y)$ was completely transferred into the organic phase.

The results of the extractions carried out with 0.05 M TTA-benzene, 0.5 M TTA-benzene, and 0.05 M TTA-hexone, respectively, are illustrated in Table II. By the extraction with TTA-benzene all the ^{90}Y was transferred into the organic phase and the ^{90}Sr remained in the aqueous phase. On the other hand, by the extraction with TTA-hexone both the ^{90}Sr and the ^{90}Y went into the organic phase. When the two-step extraction is performed, that is, when the solution is extracted first with 0.05 M TTA-benzene and then 0.05 M TTA-hexone, the latter organic phase contains ^{90}Sr alone.

The distribution coefficient and the equilibrium constant were measured at 20°C when the extraction of ^{90}Sr with TTA-hexone was performed from aqueous solution of pH 8.05. Writing the formula for TTA as HT, the reaction involved can be described by the following equation:

$$Sr^{2+}_{aq}+2HT_{org}=SrT_{2org}+2H^{+}_{aq}$$

in which subscript *org* refers to organic phase and *aq* to adueous phase. The equilibrium expression may be written as follows,

$$K=[SrT_2]_{org}\cdot[H^+]^2_{aq}/[Sr^{2+}]_{aq}\cdot[HT]^2_{org}$$

In this case the aqueous phase is a buffer solution of pH 8.05, that consists of 0.5 M ammonium acetate and aqueous ammonia, so the hydrogen ion concentration, $[H^+]_{aq}$ could be considered as being kept constant before and after the extraction. Then,

$$K'=[SrA_2]_{org}/[Sr^{2+}]_{aq}\cdot[HT]^2_{org}$$

The distribution coefficient of strontium, q, can be written as

$$q=[SrA_2]_{org}/[Sr^{2+}]_{aq}$$

so

$$K'=q/[HT]^2_{org}$$

$$\log K'=\log q-2\log[HA]_{org}$$

As the concentration of radioactive strontium is far less than that of TTA in the organic phase, $[HA]_{org}$ may be considered as being invariable during the extraction. Before the experiment, ^{90}Sr had been separated from $^{90}Sr(^{90}Y)$ by the extraction with 0.05 M TTA-benzene at pH 7 as described above, and the ^{90}Sr retained in the aqueous solution was used for the purpose. Six ml. of hexone containing TTA of various concentrations was mixed with the same volume of the aqueous solution of pH 8.05, which contained the radioactive strontium. After a separatory funnel was shaken for thirty

TABLE III

DISTRIBUTION OF ^{90}Sr BETWEEN TTA-HEXONE AND BUFFER SOLUTION OF pH 8.05, AT 20°C

Concn. of TTA in hexone M	Activity in aq. phase I_{aq} (cpm.)	Activity in org. phase I_{org} (cpm.)	Distribution coeff. q	$\log_q$	$\log K'$
0.0005	3516	126	0.03583	−1.4458	5.16
0.001	3255	104	0.03195	−1.4955	4.50
0.005	2694	840	0.3118	−0.506	4.10
0.01	2256	1422	0.6303	−0.2005	3.80
0.05	232	3495	15.065	+1.178	3.78
0.1	243	3531	14.531	+1.162	3.16
				avr.	4.08_3

TABLE IV

DISTRIBUTION OF $^{90}Sr(^{90}Y)$ BETWEEN TTA-HEXONE AND BUFFER SOLUTION OF pH 8.05, AT 20°C.

Concn. of TTA in hexone M	Activity in aq. phase. I_{aq} (cpm.)	Activity in org. phase I_{org} (cpm.)	Distribution coeff. q	$\log_q$
0.001	1778	1772	0.997	−0.0015
0.005	1486	2151	1.448	+0.1606
0.01	1156	2418	2.092	+0.3205
0.02	399	2784	6.978	+0.8437
0.04	265	3505	13.226	+1.1214
0.05	105	3364	33.04	+1.5190

minutes and the phases were disengaged, each phase was poured out through the stem and the activity measured in the ordinary way. The results are shown in Table III, from which it is found that the distribution coefficient increases with the concentration of TTA in hexone and that the 0.05 M TTA-hexone is preferable for the extraction of strontium. Table IV shows the results of the same experiments which were carried on ^{90}Sr (^{90}Y) under the same condition.

To examine the effect of the amount of strontium carrier added to the solution, extraction of $^{90}Sr(^{90}Y)$ was performed in the presence of various amounts of strontium nitrate in the buffer solution of pH 8. In this case 2 ml. of 0.05 M TTA-hexone was used as organic solvent, corresponding to 100 μg. equivalent to the chelating agent. More than 98% of the ^{90}Sr went into the organic phase in the presence of up to 1 μg. equivalent (45 μg.) of strontium carrier, and this seemed to be the upper limit of the amount of the strontium carrier that could coexist with ^{90}Sr in this extraction.

On the other hand, the extraction of ^{45}Ca with TTA-hexone was attempted in the presence of calcium carrier by the same procedure in order to obtain some information on the behavior of the metal in the solvent extraction. The calcium could be completely extracted till the amount of the carrier reached 20 μg. equivalent. Calcium seems to be chelated more tightly than strontium with TTA. The results of the above experiments are illustrated together in Fig. 2.

The effect of other alkaline earth metals —calcium, magnesium and barium—that might be present in the solution was investigated as follows. Various amounts of the metallic salt were added to the solution and the extraction of $^{90}Sr(^{90}Y)$ was done at pH 8 by 0.05 M TTA-hexone according to the above procedure. The activity of the $^{90}Sr(^{90}Y)$ separated in the organic phase was measured to find the percentage recovery of the $^{90}Sr(^{90}Y)$ in each case. Fig. 3 illustrates the relation between the amounts of the other coexisting ions and the recovery of the $^{90}Sr(^{90}Y)$. From the figure, it is found that barium and calcium do not affect the extraction till their amounts reach 8 μg. and 4 μg. equivalent, respectively, but magnesium gives a remarkable influence upon the extraction and more than 1 μg. of it should not be present.

To separate the ^{90}Sr selectively into the organic phase from the $^{90}Sr(^{90}Y)$, the solution containing $^{90}Sr(^{90}Y)$ was first adjusted to pH 7, and the extraction was done with 0.05 M TTA-benzene, by which ^{90}Y could be completely transferred out of the solution into the organic phase as shown in Table V. The aqueous phase retained after the extraction was adjusted again to pH 8, and a second extraction was done with 0.05 M TTA-hexone. Thus

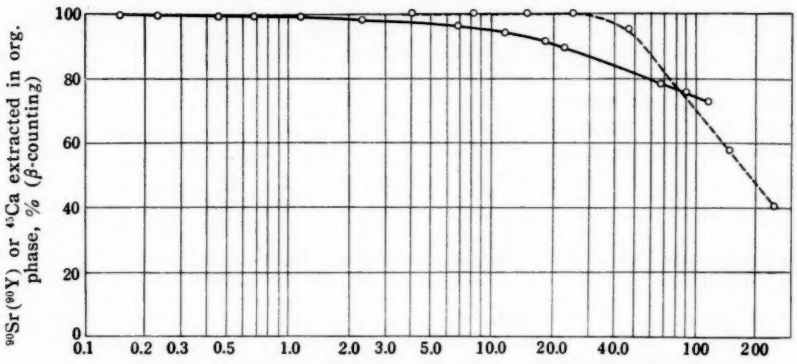

Fig. 2. Effect of strontium carrier on the extraction of ^{90}Sr(^{90}Y) and of calcium carrier on the extraction of ^{45}Ca by TTA-hexone.
—— strontium, ... calcium

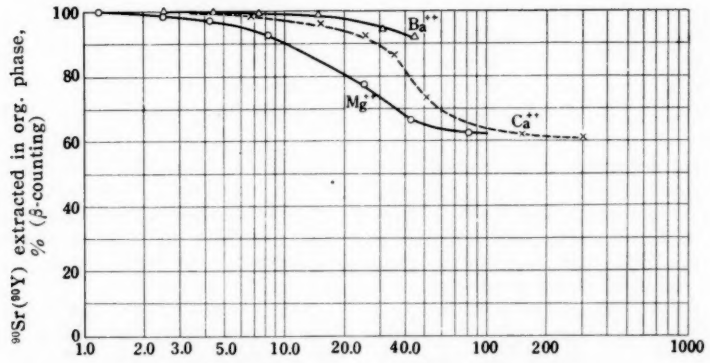

Fig. 3. Effect of the amounts of coexisting alkaline earth metals on the extraction of ^{90}Sr(^{90}Y) by TTA-hexone.

TABLE V

ISOLATION OF ^{90}Sr FROM ^{90}Sr(^{90}Y) BY THE TWO-STEP EXTRACTION

^{90}Sr(^{90}Y) taken cpm.	Taken up by the 1st org. phase (0.05 M TTA-benzene at pH 7) cpm.	Taken up by the 2nd org. phase (0.05 M TTA-hexone at pH 8) cpm.	Retained in aq. phase cpm.
16,590	8,890	7,186	510
17,050	9,440	7,328	280
Radiochemical purity (^{90}Y: 99%)		(^{90}Sr: 100%)	

the strontium could be separated in the last organic phase. Table V shows the excellent results of the extraction.

The presence of a masking agent such as EDTA (disodium ethylenediaminetetra-acetate), and ammonium citrate may probably affect the extraction of ^{90}Sr(^{90}Y).

Investigation was carried out to test this view, and was unsuccessful to keep the calcium in the solution by the masking effect of EDTA and to transfer the strontium into the organic phase; moreover, even the extraction of yttrium into the organic phase was markedly hindered. When a buffer solution consisting of ammonium citrate and aqueous ammonia was used to keep the solution at pH 8, only ^{90}Y could be extracted into the organic phase of TTA-hexone. The results obtained are shown in Table VI.

TABLE VI

EFFECT OF THE MASKING AGENTS ON THE EXTRACTION OF $^{90}Sr(^{90}Y)$ BY TTA-HEXONE

$^{90}Sr(^{90}Y)$ taken cpm.	Ca^{2+} added μg.	EDTA added ml.	Extracted into org. phase %	Nuclide extracted
6,980	2,000	1	4.8_1	^{90}Y
7,040	1,000	1	9.1_2	〃
7,110	800	1	6.2_0	〃
6,890	400	1	2.8_1	〃
7,080	1,000	2	2.6_1	〃
6,650	600	2	1.5_6	〃

Note: One milli liter of EDTA solution corresponds to 566 μg. Ca^{2+}.

$^{90}Sr(^{90}Y)$ taken cpm.	0.1 M Ammonium citrate soln. ml.	Extracted in org. phase %	Nuclide extracted
7,600	5	60.52	^{90}Y
18,800	5	55.67	〃

TABLE VII

ISOLATION OF RADIOACTIVE STRONTIUM BY TWO-STEP EXTRACTION FROM THE MIXED FISSION PRODUCTS

The fission products taken cpm.	Extracted by 0.05 M TTA-benzene cpm.	Extracted by 0.05 M TTA-hexone cpm.	Retained in aq. phase cpm.
57,980	48,640	6,260(10.8%)	3,080
56,980	48,550	5,960(10.4%)	2,470
120,900	102,500	12,370(10.2%)	6,050

In order to separate the radioactive strontium from mixed fission products, the solution of the material was at first adjusted to pH 7 and extracted with 0.05 M TTA-benzene. By this treatment rare earths and yttrium were made go into the organic phase out of the solution, but ruthenium was not. The aqueous phase remaining after the extraction and the removal of the organic phase, was transferred into another separatory funnel, and adjusted to pH 8 with the addition of ammonia, and extracted with 0.05 M TTA-hexone. In this case the radioactive strontium was completely extracted into the organic phase. Only less than 5% of ruthenium presented in the solution was extracted together.

The organic phase containing radioactive strontium was transferred from the funnel into a counting pan and rapidly evaporated to dryness under an infrared lamp, and the activity was measured as usual. The results obtained are shown in Table VII, in which the percentage of the strontium, represented by the activity ratio to the total, coincides well with that obtained by the ion-exchange resin method for the separation of the same material[5].

The Harley plot for the activity of the separated strontium is shown in Fig. 4 with ^{32}P as standard. The plot indicates that the radioactive strontium consists of 64% ^{89}Sr and 36% ^{90}Sr. The above separation process can be performed without spending much time.

The strontium extracted in the organic phase can easily be taken in the solution by the stripping with nitric acid of various concentrations. However, as the evaporation of the organic phase of TTA-hexone proceeds rapidly under an infrared lamp, the stripping of the strontium seems unnecessary for the purpose. Thus, by

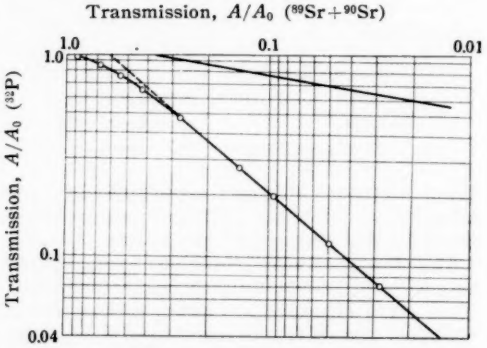

Fig. 4. Harley plot of the radioactive strontium separated in TTA-hexone from the gross fission products.

5) M. Honda, Y. Sasaki and H. Natsume, *Japan Analyst (Bunseki Kagaku)*, 4, 240 (1955).

the two-step extraction method devised by the authors, radioactive strontium could be separated rapidly and efficiently from mixed fission products.

Summary

Radioactive strontium in mixed fission products could be rapidly separated by the two-step extraction deviced by the authors. The solution of the material was first adjusted to pH 7 and extracted with 0.05 M TTA-benzene. By this treatment rare earths and yttrium were made to go into the organic phase out of the solution. The remaining aqueous phase was transferred into another separatory funnel, adjusted to pH 8, and extracted with 0.05 M TTA-hexone. In this case the radioactive strontium was completely extracted into the organic phase. Only less than 5% of ruthenium present in the solution was extracted at the same time. Detailed data of the experiments on the extraction involving the determination of distribution coefficient, and the equilibrium constant were tabullated.

This study was done as a part of the co-operative research on the radiochemical studies of the fission products and a part of the expenses was defrayed by a grant from the Ministry of Education, to which the authors' thanks are due.

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Separation of Fission Products by Liquid-Liquid Extraction with Cupferron-Chloroform

By Toshiyasu KIBA and Mitsue KANETANI

(Received May 30, 1958)

Workers in various fields of study are looking for methods of rapidly separating radioactive strontium and cesium from solutions containing fission products. Before such separation is attempted, preliminary elimination of other nuclides and non-radioactive ions must be accomplished. When the precipitation method is employed for this purpose, some carrier must be added to the solution and some loss of the radioactive elements in question results from adsorption by the precipitate. Also the method takes a considerable length of time.

The solvent extraction method can be carried out rapidly and simply without any carrier. The aim of the investigation described in this paper was to establish a new method of liquid-liquid extraction by which the radioactive strontium and cesium are retained in the aqueous solution, while other metallic ions are transferred into the organic phase. The strontium and cesium may be further separated conveniently by the TTA-hexone extraction method as described in another paper by the present authors. The extracting agent for this purpose should be a compound which easily combines with various metallic ions, and forms chelated compounds, readily soluble in some organic solvent. Cupferron was chosen for the purpose for this reason.

Cupferron (nitrosophenyl hydroxylamine) is easily obtainable as an ammonium salt, which is a common reagent; it forms chelated compounds with zirconium in strong acids[1], with ter- to quinqui-valent metallic ions in weakly acidified solutions[2], and with rare earths in solutions whose pH is between 3 to 4[3], and produces precipitate when large amounts of these ions are present. Both the reagent and the chelated compounds are soluble in chloroform, with which they are easily removed from the aqueous solution. These characteristics of the

1) N. H. Furman, W. B. Marson and J. S. Pekola, *Anal. Chem.*, **21**, 1355 (1949).
2) D. Dyrssen and V. Dahlberg, *Acta Chim. Scand.*, **7**, 1186 (1953).
3) A. I. Popov and W. W. Wendlandt, *Anal. Chem.*, **26**, 883 (1954).

reagent were found very useful in the treatment of an aqueous solution containing fission products.

Experimental

Reagent and apparatus.—*Cupferron Solution*, 5%.—The reagent of extra pure grade was dissolved in water immediately before use.

Gross Fission Products.—A drop of nitric acid solution of gross fission products, imported from Oak Ridge National Laboratory, U. S. A. (Batch No. 35; cooling period, about three years) was diluted with 0.02 N hydrochloric acid so that 0.2 ml. of the solution possesed an activity of 10,000 cpm.

Other Radioisotopes.—^{90}Sr(^{90}Y), ^{95}Zr(^{95}Nb), ^{137}Cs, ^{106}Ru(^{106}Rh), ^{144}Ce, and ^{147}Pm were used and their behavior during the solvent extraction with cupferron was examined.

Buffer Solution.—0.5 M solution consisting of acetic acid, ammonium acetate, and aqueous ammonia was used, and the pH was measured by a glass electrode pH-meter.

Activity Measurement.—For β-radiation, a counting set made by the Kobe Kogyo Co. Ltd., Japan (No. 131 G-M tube: mica window, 2.2 mg./cm^2, counting efficiency: 11.7% for ^{90}Sr(^{90}Y)) was employed; for γ-radiation, a counting set made by Nuclear Instrumental and Chemical Corp., U. S. A., (sodium iodide scintillation tube, and Model D 47 counting equipment with lead absorber) was used.

Separatory Funnel.—A 30 ml. and a 300 ml. spindle shaped separatory funnel having a big short stem were used for good separation of the two phases.

Shaking Machine.—Shaking was effected by a vertical electric oscillator with 230 double strokes per minute. Up to six separatory funnels can be loaded on the shaker at a time.

Other chemicals used were all of extra pure grade and the utensils were of the ordinary laboratory type.

Procedure.—1) In a 30 ml. separatory funnel place 0.2 ml. of a solution of the gross fission products or radioisotopes, and 5 ml. of 1 to 7 N hydrochloric acid or 5 ml. of the buffer solution, and make up the volume with water to 6 ml. Then, add 1 ml. of the cupferron solution and 2 ml. of chloroform, successively. Shake the contents of the vessel for five minutes. After the phases have disengaged, transfer the organic phase into another funnel and add to it 5 ml. of hydrochloric acid or the buffer solution, and shake with the organic phase for five minutes. To the aqueous phase retained in the first funnel add again 1 ml. of the cupferron solution and 2 ml. of chloroform, and shake for five minutes. Combine the aqueous phases from the first and the second funnel in a centrifuge tube, and the organic phases in another tube and centrifuge them for about two minutes to separate the phases completely from each other. Transfer each phase to a porcelain counting dish and evaporate to dryness under an infrared lamp, and then measure the radioactivity by the counting set. Draw off the decay and the Harley plot of the activity, if necessary, to identify the nuclide isolated.

2) When various metallic ions other than fission products are present, the following procedure was adopted, by which the radioactive strontium and cesium were retained in the solution unaccompanied by other metallic ions.

Put 100 ml. of a solution containing 10 mg. of iron(III), thorium(IV), and uranyl(II) ions and fission products in a 350 ml. separatory funnel, and adjust its acidity to 1 N hydrochloric acid. Add 2 ml. of the cupferron solution and 5 ml. of chloroform, and shake for five minutes. Take out the organic phase from the first funnel and retain the aqueous phase in the vessel. Repeat the same extraction process in the first funnel till further addition of the cupferron solution produces no precipitate and the aqueous phase becomes colorless. The organic phase separated after each extraction should be collected in another funnel and washed with an equal volume of 1 N hydrochloric acid. The washing should be added to the solution in the first funnel. By this process, iron(III) is completely removed from the solution.

After the removal of iron(III), add 3 N hydrochloric acid to restore to 1 N hydrochloric acid the acidity of the solution, which has been lowered by the successive entrainments of the cupferron solution. Add 2 ml. of the cupferron solution and 10 ml. of ethyl acetate, and shake for two or three minutes. Drain the aqueous phase from the first funnel into the second, and repeat the extraction with cupferron and ethyl acetate. Collect the ethyl acetate phase retained in each extraction in the first funnel and wash the contents with an equal volume of hydrochloric acid. Add the washings to the solution in the third funnel. Thorium(IV) is transfered to the ethyl acetate phase by this extraction.

Add 20 ml. of 3% zinc amalgam to the solution in the second or the third separatory funnel, stopper well, and shake vigorously for five minutes to reduce the uranyl ion which does not combine with cupferron to uranium(IV). After removing the amalgam through the stem, add 2 N aqueous ammonia drop by drop till the pH of the solution becomes 1.8. Then add 2 ml. of the cupferron solution and 10 ml. chloroform, and shake the content for five minutes. Repeat the extraction till further addition of cupferron produces no precipitate. By this treatment the uranium is completely removed, going into the organic phase that is discarded after the extraction.

Add 2 N aqueous ammonia to the solution retained in the separatory funnel to adjust the pH to 4. Add again 2 ml. of the cupferron solution and 10 ml. chloroform, and shake for five minutes. By the last extraction rare earths of the fission products and non-radioactive metals are transferred into the chloroform phase. If necessary, repeat the extraction.

The separated aqueous phase which contains the radioactive strontium and cesium and possibly

some unextractable cations, may be given additional treatments of separation, for example, with TTA-hexone.

3) The behavior of the various radioisotopes were examined throughout all the stages of the extraction described above, and the percentages of the nuclides recovered were noted.

Results and Discussion

After the extraction was carried out by Procedure 1 on the aqueous solution of the gross fission products at different pH, the separated organic phase was evaporated to dryness and the radioactivity was measured by means of a G-M β-counting set. The ratio of the counting rate (cpm.) of the organic phase to that of the original solution represents the amount extracted of the gross fission products. As illustrated in Fig. 1, the

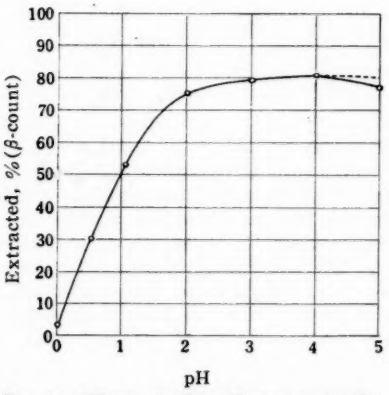

Fig. 1. Effect of pH on the extractability of gross fission products by cupferron-chloroform.

ratio reaches its maximum of 81% at pH 4 and decreases slightly as the pH of the solution increases still further, probably because of formation of radiocolloid in the solution. Evaporation of the chloroform containing cupferron may be readily accomplished with an infrared lamp, and the residue transformed into the oxide by ignition to red heat. Therefore, the stripping of the nuclide from the organic phase was not found necessary.

To find what nuclides could be extracted from the mixed gross fission products into the organic phase, the extraction was done with the solution containing ^{106}Ru, ^{137}Cs, ^{90}Sr(^{90}Y), and rare earths that had been separated as a fraction of the fission products by the cation exchange resin method[4]. The results of the experiments for each nuclide is shown in Fig. 2., from which it is found that rare earths and yttrium go into the organic phase at pH 4, and cesium, strontium and ruthenium remain in the solution.

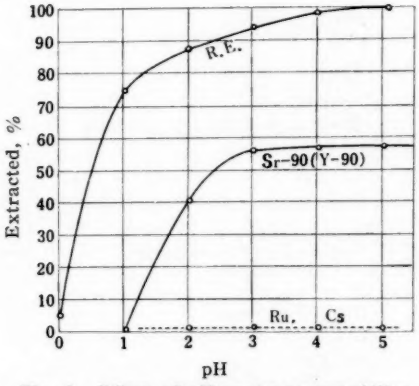

Fig. 2. Effect of pH on the extractability of some nuclides in fission products by cupferron-chloroform.

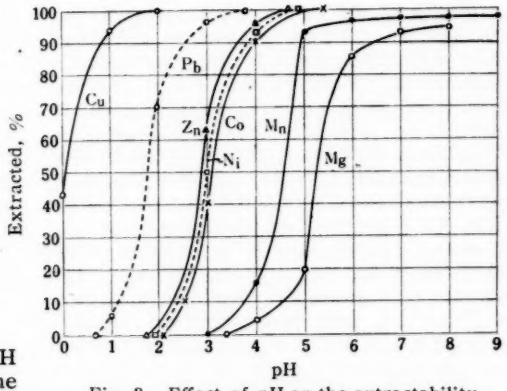

Fig. 3. Effect of pH on the extractability of various metallic ions by cupferron-chloroform.

The extraction of other non-radioactive metallic ions at different pH is shown in Fig. 3. Many ions can be removed into the cupferron-chloroform while the acidity of the solution is higher than pH 4.

One hundred ml. of the solution containing the gross fission products together with iron(III), thorium(IV), and uranyl(II) ions, was treated by successive extractions of Procedure 2. The aqueous phase

4) M. Honda, Y. Sasaki and H. Natsume, *Japan Analyst (Bunseki Kagaku)*, **4**, 240 (1955).

TABLE I

EXTRACTION OF FISSION PRODUCTS AND RADIOISOTOPES BY CUPFERRON-CHLOROFORM

Amounts taken or original radioactivity	Percentage of radioactivity in the last aqueous phase %
Fe(III) : 10 mg. Fission products : 10,000 cpm.	18.05(^{90}Sr and ^{137}Cs)
Fe(III) : 10 mg. ^{137}Cs : 10,000 cpm.	100. (^{137}Cs)
Fe(III) : 10 mg. ^{90}Sr(^{90}Y) : 10,000 cpm.	42.5 (^{90}Sr)
Fe(III) : 10 mg. U(VI) : 5 mg. Th(IV) : 10 mg. Fission products : 10,000 cpm.	20.3 (^{90}Sr, ^{137}Cs and ^{106}Ru) 15.9 (after the Ru was expeled by distillation)

TABLE II

RESULTS OF TWO-STEP EXTRACTION WITH CUPFERRON-CHLOROFORM AND TTA-HEXONE

Material taken or original radioactivity in original solution	Percentage of radioactivity extracted in TTA-hexone phase %	Percentage of radioactivity retained in the last aq. phase %
Fe(III) : 10 mg. ^{137}Cs : ca. 10,000 cpm.	0.	100.
Fe(III) : 10 mg. ^{90}Sr(^{90}Y) : 10,000 cpm.	42.1 (^{90}Sr)	0.36 (^{90}Sr)
Fe(III) : 10 mg. ^{106}Ru : ca. 10,000 cpm.	1.5 (^{106}Ru)	97.9 (^{106}Ru)

remaining at the end was evaporated and the radioactivity was measured to determine the recovery of the radioactive substances. Very satisfactory results were obtained in each case as shown in Table I.

The aqueous phase remaining after the solvent extraction with cupferron-chloroform was next subjected to treatment with TTA-hexone as described in the following paper, and strontium was extracted into the organic phase. The two-step extraction gave the results shown in Table II, and the strontium in the original solution could be separated rapidly and quantitatively from the gross fission products.

Summary

In order to separate rapidly the radioactive strontium and cesium from the solution containing gross fission products and other non-radioactive metallic ions, cupferron-chloroform extraction was attempted. By changing the acidity of the aqueous solution from 1 N hydrochloric acid to pH 4, and by performing extractions in each stage, the strontium and the cesium could remain in the aqueous phase, while the other could be removed into the organic phase. The radioactive strontium may be extracted in the organic phase by the following extraction with TTA-hexone at pH 8.

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Metal Complexes with Terdentate Ligands. I. Synthesis of Copper(II) and Nickel(II) Complexes having Salicylaldehydesemicarbazone and Related Compounds as Ligands

By Yoneichiro MUTO

(Received June 6, 1958)

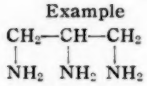
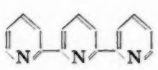
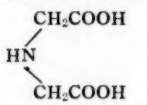
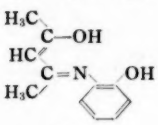
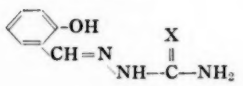
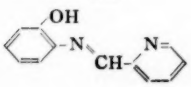
In marked contrast with the extensive studies that have been carried out on the metal complexes with terdentate ligands, those with terdentate ligands have received much less attention. The latters are of particular interest in coordination chemistry because of their steric requirements. A few examples of the terdentate chelating agents of types I and II are shown in Table I. The chelating agents of type III, while satisfying one primary valence of the metal, fill three coordination positions. The examples of type III are comparatively meagre.

It has been reported that a thiosemicarbazide molecule occupies two coordination positions of platinum(II)[1], palladium (II)[1], cobalt(II)[2], copper(II)[2] and nickel[2] ions* and that some thiosemicarbazones coordinate to copper(II)- and nickel ions as a bidentate ligand[3]. Semicarbazide forms complexes having the compositions, $CH_5ON_3CuCl_2$ and $(CH_5ON_3)_2NiSO_4$[4]. It is likely that a semicarbazide molecule occupies two coordination positions of copper(II) and nickel. Therefore, it is expected that semicarbazone or thiosemicarbazone of salicylaldehyde acts as a terdentate ligand of type II (in enol form) or type III (in keto form) and that *α*-pyridylaldehyde-*o*-hydroxyanil similarly acts as a ligand of type III. The present author synthesized copper(II) and nickel complexes having the ligands shown in Table II.

Salicylaldehydesemicarbazone was treated with copper(II) salts in a boiling ethanol solution. Depending on the kind of copper(II) salt, the copper(II) complexes of two different types were formed in the following way.

From the chemical analysis and the properties of the complex as well as the terdentate nature of the ligand, it seems reasonable to give the formula A to salicylaldehydesemicarbazone copper(II), although no direct evidence has yet been afforded by physical methods such as X-ray analysis. Similarly, the formula B has been presumed for salicylaldehydesemi-

TABLE I

Types	Example	
I. A-A-A[a]		
II. HA-A-AH[b]		
III. HA-A-A	 (X: O, S.)	

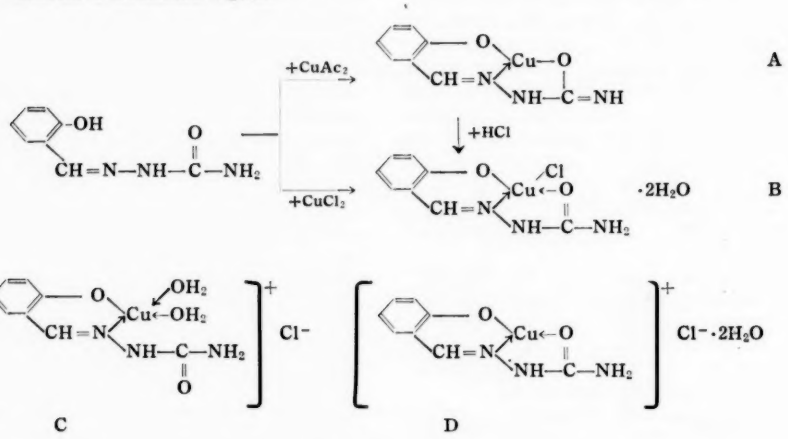
a) A: a donor atom such as N, O and S. b) H: a hydrogen atom replaceable with metal atom. c) the enol form of acetylacetonemono-(2-hydroxyanil). Y. Muto, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zassi*), **76**, 1407 (1955).

1) K. A. Jensen, *Z. anorg. allgem. Chem.*, **221**, 6 (1934).
2) K. A. Jensen and E. Ranke-Madsen, ibid., **219**, 243 (1934).
3) G. Bähr and E. Hess, ibid., **268**, 351 (1952).
4) K. A. Jensen and E. Ranke-Madsen, ibid., **227**, 25 (1936).

TABLE II

	Chelating agents (A)*	Composition of the complex	Solubility of the complex
1.	Salicylaldehydesemicarbazone	Cu(A)	Insol. in H_2O, EtOH, benzene. Sol. in pyridine.
		$Cu(A)NH_3$	Insol. in H_2O, benzene. Sol. in EtOH.
		$Cu(A)Cl\cdot 2H_2O$	Insol. in EtOH, benzene. Sol. in H_2O.
		$Cu(A)NO_3$	the same as the above
		$Ni(A)_2\cdot H_2O$	Insol. in H_2O, EtOH, benzene, pyridine.
2.	5-Bromosalicylaldehydesemicarbazone	Cu(A)	Insol. in H_2O, EtOH, benzene.
		Cu(A)Cl	Insol. in EtOH, benzene. Slightly sol. in H_2O.
3.	Salicylaldehydethiosemicarbazone	Cu(A)	Insol. in H_2O, EtOH, benzene. Sol. in pyridine.
		Cu(A)py	Insol. in H_2O. Slightly sol. in EtOH.
		$Cu(A)Cl\cdot H_2O$	Insol. in EtOH, benzene. Slightly sol. in H_2O.
		Ni(A)py	Insol. in H_2O. Slightly sol. in EtOH.
		$Ni(A)_2\cdot 2H_2O$	Insol. in H_2O, EtOH, benzene. Sol. in pyridine.
4.	α-Pyridylaldehyde-o-hydroxyanil	$Cu(A)Cl\cdot 2H_2O$	Sol. in H_2O, EtOH, $CHCl_3$, nitrobenzene.
		$Cu(A)NO_3\cdot 2H_2O$	the same as the above

* "A" denotes a terdentate ligand.



A B C D

carbazone-monochloro copper(II) dihydrate for the following reasons. First, if salicylaldehydesemicarbazone were assumed to act as a bidentate ligand for a copper(II) ion, the chelate compounds with the molar ratio 1:2 of copper(II) to the reagent molecule should be formed just as in the case of Shiff's base prepared from salicylaldehyde and various primary amines. However, the composition of this complex and other copper(II) complexes obtained in this work had the molar ratio 1:1 of copper(II) to the reagent molecule as shown in Table II. Therefore, this reagent must occupy three coordination positions of a copper (II) ion. Secondly, from the fact that the water molecules contained in this complex could easily be removed by drying in a desiccator over calcium chloride at room temperature, it seems very likely

that the water molecules do not coordinate directly to the copper atom. Thirdly, provided that the coordination number of copper(II) is four as usual, another unidentate ligand is required to fill the inner sphere around the copper atom which has already a terdentate ligand combined with it. Furthermore, the electric conductivity of dilute aqueous solutions of this complex was found to be small. Therefore, the chlorine atom is considered as being in the inner sphere around the copper atom, and it seems unlikely that this complex has a salt-like structure as shown in the formula C or D.

Experimental

1) **Salicylaldehydesemicarbazone copper (II).**—A solution of copper acetate monohydrate (0.6 g.) in water (30 ml.) was added to a boiling solution of salicylaldehydesemicarbazone (0.55 g.) in ethanol (50 ml.). Pale green micro crystals immediately precipitated. This precipitate was purified in the following way. The precipitate was dissolved in a mixture of ethanol (20 ml.) and aqueous ammonia (28%, 2 ml.) and then 10 ml. of water was added to it. The greenish solution was allowed to cool at room temperature for about three hours; mean while the addition compound with ammonia crystallized in gray prismatic crystals. The separated crystal was heated at 60~70°C until ammonia was no longer evolved. To ensure the complete removal of ammonia, the residue was boiled in ethanol on a water bath for ten minutes. After being allowed to cool, the precipitate was filtered off and dried at about 80°C.

Anal. Found: C, 39.92; H, 2.93; N, 17.46; Cu, 26.38%. Calcd. for $C_8H_7O_2N_3Cu$: C, 40.01; H, 3.15; N, 17.36; Cu, 26.19%.

The addition compound with ammonia liberates ammonia gradually at room temperature; hence the analysis was performed without delay after preparation.

Anal. Found: N, 21.70; Cu, 24.69; NH_3, 6.44%. Calcd. for $C_8H_7O_2N_3Cu \cdot NH_3$: N, 21.74; Cu, 24.65; NH_3, 6.61%.

2) **Salicylaldehydesemicarbazone - monochloro copper(II) dihydrate.**—A hot solution of copper(II) chloride dihydrate (0.5 g.) in water (10 ml.) was added to a hot solution of salicylaldehydesemicarbazone (0.5 g.) in ethanol (20 ml.). The greenish solution was allowed to stand overnight at room temperature. The green precipitate formed was washed with ethanol. The pure compound was obtained in deep green prismatic crystals by recrystallization from water. The hydrate lost water gradually in a desiccator over calcium chloride and was completely dry at 50~60°C. The color of the crystals became brown after dehydration.

Anal. Found: C, 30.77; H, 3.79; N, 13.73; Cl, 11.23; Cu, 20.34; H_2O, 11.40%. Calcd. for $C_8H_8O_2N_3ClCu \cdot 2H_2O$: C, 30.68; H, 3.94; N, 13.70; Cl, 11.32; Cu, 20.29; H_2O, 11.50%.

This compound was also obtained by heating the compound prepared in 1) with dilute hydrochloric acid on a water bath.

3) **Salicylaldehydesemicarbazone - mononitrato copper(II).**—This compound was prepared in the same way as the monochloro compound by the reaction between salicylaldehydesemicarbazone and copper(II) nitrate. The green crystals formed were dried in a desiccator over calcium chloride at room temperature.

Anal. Found: N, 18.51; Cu, 20.77%. Calcd. for $C_8H_8O_5N_4Cu$: N, 18.45; Cu, 20.92%.

4) **Bis-salicylaldehydesemicarbazone nickel monohydrate.**—A solution of nickel acetate tetrahydrate (0.5 g.) in water (10 ml.) was added to a boiling solution of salicylaldehydesemicarbazone (0.7 g.) in ethanol (40 ml.). Light green prismatic crystals were immediately precipitated. The separated crystals were washed with hot ethanol, then with pyridine and finally with hot water and they were dried in a vacuum desiccator. The corresponding nickel complex was not formed by the reaction between nickel sulfate and salicylaldehydesemicarbazone although the solutions were mixed in the same way as described above.

Anal. Found: N, 19.31; Ni, 13.7%. Calcd. for $C_{16}H_{16}O_4N_6Ni \cdot H_2O$: N, 19.41; Ni, 13.6%.

5) **5-Bromosalicylaldehydesemicarbazone copper(II).**—This compound was prepared as pale green micro crystals in the same way as the compound described in 1).

Anal. Found: N, 13.38; Cu, 19.92%. Calcd. for $C_8H_6O_2N_3BrCu$: N, 13.15; Cu, 19.88%.

6) **5-Bromosalicylaldehydesemicarbazone-monochloro copper (II).**—This compound was prepared in the same way as the compound described in 2). The gray crystals formed were dried in a desiccator over calcium chloride at room temperature.

Anal. Found: N, 11.86; Cu, 17.80%. Calcd. for $C_8H_7O_2N_3ClBrCu$: N, 11.80; Cu, 17.84%.

7) **Salicylaldehydethiosemicarbazone copper(II).**[5]—This compound was prepared in the same way as the compound described in 1). The brown crystals formed were dried at 60°C.

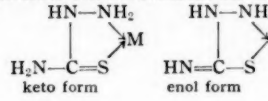
Anal. Found: C, 37.62; H, 3.10; N, 16.41; Cu, 24.74%. Calcd. for $C_8H_7ON_3SCu$: C, 37.42; H, 2.75; N, 16.36; Cu, 24.75%.

The pyridinate of this copper complex was obtained as pale brown needles by recrystallizing it from pyridine.

Anal. Found: N, 16.71; Cu, 19.02; pyridine, 23.49%. Calcd. for $C_8H_7ON_3SCu \cdot C_5H_5N$: N, 16.68; Cu, 18.92; pyridine, 23.55%.

8) **Salicylaldehydethiosemicarbazone-monochloro copper(II) monohydrate.**—This compound was prepared in the same way as the

5) V. Hovorka and Z. Holzbecher, *Collection Czechoslov. Chem. Communs.*, **15**, 267 (1950).

* 

M: bivalent metal.

compound described in 2). Green prismatic crystals.

Anal. Found: N, 13.68; Cu, 20.23%. Calcd. for $C_8H_9ON_3SClCu \cdot H_2O$: N, 13.50; Cu, 20.41%.

9) **Monopyridino-salicylaldehydethiosemicarbazone nickel.**—A solution of nickel acetate tetrahydrate (0.5 g.) in water (10 ml.) was added to a boiling solution of salicylaldehydethiosemicarbazone (0.4 g.) in ethanol (30 ml.). Orange crystals were precipitated immediately. The separated precipitate was dissolved in pyridine and filtered. When water was added to the filtrate, the monopyridino compound separated out as brown-red needles.

Anal. Found: N, 16.92; Ni, 17.6; pyridine, 23.12%. Calcd. for $C_8H_7ON_3SNi \cdot C_5H_5N$: N, 16.93; Ni, 17.7; pyridine, 23.90%.

10) **Bis-salicylaldehydethiosemicarbazone nickel dihydrate.**—A hot solution of nickel sulfate heptahydrate (0.3 g.) in water (5 ml.) was added to a boiling solution of salicylaldehydethiosemicarbazone (0.4 g.) in ethanol (50 ml.). Light green crystals were precipitated immediately. The separated precipitate was boiled in ethanol on a water bath, filtered off and washed by hot water. This procedure was repeated two or three times, and then the crystals were dried in a vacuum desiccator.

Anal. Found: N, 17.67; Ni, 12.08%. Calcd. for $C_{16}H_{16}O_2N_6S_2Ni \cdot 2H_2O$: N, 17.40; Ni, 12.10%.

When this compound was recrystallized from pyridine, the monopyridino compound described in 9) was formed.

11) **α - Pyridylaldehyde - *o* - hydroxyanil-monochloro copper (II) dihydrate.**— This compound was prepared in the same way as the compound described in 2) by the reaction between copper(II) chloride and α-pyridylaldehyde-*o*-hydroxyanil. Brown-black prismatic crystals.

Anal. Found: C, 43.70; H, 4.00; N, 8.22; Cu, 19.07; H_2O, 10.80%. Calcd. for $C_{12}H_9ON_2ClCu \cdot 2H_2O$: C, 43.40; H, 3.95; N, 8.44; Cu, 19.12; H_2O, 10.84%.

12) **α - Pyridylaldehyde - *o* - hydroxyanil-mononitrato copper (II) dihydrate.** — This compound was prepared in the same way as the compound described in 2) by the reaction between copper nitrate and α-pyridylaldehyde-*o*-hydroxyanil. Brown-black prismatic crystals.

Anal. Found: N, 11.60; Cu, 17.63; H_2O, 10.01%. Calcd. for $C_{12}H_9O_4N_3Cu \cdot 2H_2O$: N, 11.71; Cu, 17.71; H_2O, 10.04%.

13) **Electric conductance of copper (II) complexes.**—The concentration of the solution used for measurement at 15°C was 0.001 M. The results were listed in Table III.

TABLE III

Compound	Molar conductance (mho)
1. Salicylaldehydesemicarbazone -monochloro copper(II) dihydrate	30.5
2. Salicylaldehydesemicarbazone -mononitrato copper(II)	32.5
3. α-Pyridylaldehyde-*o*-hydroxyanil -monochloro copper(II) dihydrate	30.7
4. α-Pyridylaldehyde-*o*-hydroxyanil -mononitrato copper(II) dihydrate	30.5

The pH values of these solutions were found to be 5.4~6.3. Therefore, it is possible that these complexes decompose to some extent in water. This accounts for such a low yield as 50% of the recrystallization of these complexes from water.

The author is grateful to Mr. Michio Shido of Kyushu University for carrying out the elementary analysis of the compounds prepared.

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*Chemical Studies on Wood Hemicelluloses. II. On the Hemicellulose of Ganpi Bast Fibres. I**

By Seishi MACHIDA and Sadanori NISHIKORI**

(Received June 13, 1958)

Wood hemicelluloses, which have generally undesirable influences upon the manufacture and qualities of chemica lfibres, are said to have rather favorable effects on paper-making[1].

Cottrall[2] investigated the bearing of hemicelluloses of wood pulp fibres on paper-making properties, and assented that the excellent character of Japanese hand-made paper could be attributed to the peculiar method of paper-making. The Japanese hand-made paper which has elegant and strong quality, is made in the traditional manner. Bast fibres of certain plants are used as the raw material and the extracted juice of various plant roots and barks are employed as sizing and dispersing agents[3].

The present investigation, therefore, was attempted to explain the behavior of hemicellulose during the processes of Japanese paper-making. The relation between the chemical characteristic of the hemicellulose and the paper-making properties of the fibres was also investigated.

Experimental

1) Sample.—The bast fibres used in the present study were obtained from the Ganpi plant (*Wickstroemia sikokiana* Franch. et Sav.) grown in Simane Prefecture. Ganpi, a species of *Thymelaeaceae*, is a wild shrub growing widely in Japan, and the paper made from it is one of the most typical hand-made papers of Japan. The bast fibres removed from the plant stems were cleaned by removing the upper brown cork tissue and flawed parts, washed sufficiently with water, and dried.

2) Process of paper-making.—The bast fibres thus purified were boiled with a sodium carbonate solution, in which the concentration of sodium carbonate is 20% of that of the pulp, and washed in a stream to remove the meterial formed by the reaction with alkali for two days. In the stream the fibres are also mildly bleached.

Next, the fibres were beaten for about an hour in a beater. The rotation of the beater-roll is about 150 r. p. m.; pulp concentration is about 3%. The degree of beating of the resultant pulp estimated with Schopper-Riegler's tester was 25. The paper was made from the pulp by the hand process in the usual manner of Japanese paper-making, using the mucilage of the Tororo-aoi plant[4] as the dispersing and sizing agent.

3) Chemical constituents of the fibres in the process of paper-making.—The samples from the various stages of the process were analysed in the usual manner[5]. The results obtained are shown in Table I.

4) Hemicellulose of the Ganpi plant.—Hemicellulose fractions were obtained by alkaline extraction of holocelluloses prepared from Ganpi bast fibres. These fibres finely chopped were extracted with benzene-ethanol, filtered and air dried prior to use. From this sample, holocellulose was prepared by Wise's method[6]. Yield was 87.0%. Hemicellulose fractions were extracted from the holocellulose with sodium hydroxide solution. Successive extractions with the 5 and 16% solution for periods of an hour at room temperature yielded two fractions; these hemicellulose fractions were designated "5% extract" and "16% extract", respectively. The solid hemicelluloses were recovered from the alkaline solutions by pouring the latter into 4 volumes of ethanol containing sufficient acetic acid to adjust the pH to about 6.5. The flocculent precipitate was centrifuged, washed with ethanol and ether, and then dried in a desiccator.

The dilute solution viscosity of the water-soluble "5% extract" in distilled water was measured and a plot of the reduced specific viscosity against concentration is represented by the upper curve of Fig. 1. In the $\eta_{sp}/c \sim C$ curve, a significant polyelectrolyte behavior of the hemicellulose is indicated. The lower curves of Fig. 1 are the $\eta_{sp}/c \sim C$ curves for the hemicelluloses in 10% potassium hydroxide solution

* The principal part of this paper was presented at the 11th Annual Meeting of the Chemical Society of Japan on April 5, 1958 at Tokyo.

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1) M. N. Fineman, *Tappi*, **35**, 320 (1952).

2) L. G. Cottrall, "World's Paper Trade Rev.", 393, 445 (1954).

3) S. Machida and M. Inano, This Bulletin, **28**, 629 (1955).

4) S. Machida and N. Uchino, *Bull. of the Faculty of Textile Fibres, Kyoto Univ. of Ind. Arts & Text. Fibres*, **1**, 116 (1954).

5) S. Machida, M. Inano and Y. Matsumura, This Bulletin, **30**, 201 (1957).

6) L. E. Wise and E. K. Ratliff, *Anal. Chem.*, **19**, 459 (1947).

7) J. O. Thompson and L. E. Wise, *Tappi*, **35**, 331 (1952).

TABLE I
COMPOSITION OF BAST FIBRES OF GANPI PLANT

	Original raw bast fibre	Pulp after alkali-cooking	Pulp after wet beating	Paper
Moisture	13.90%	10.98%	11.39%	11.51%
Ash	1.84〃	1.86〃	1.29〃	1.57〃
Benzene-Ethanol extract	2.11〃	1.71〃	1.62〃	1.85〃
Cold water extract	2.84〃	2.68〃	0.81〃	1.97〃
Hot water extract	6.03〃	3.48〃	1.32〃	2.43〃
0.1% NaOH extract	15.54〃	4.46〃	3.74〃	5.49〃
Lignin	3.30〃	2.77〃	2.80〃	2.89〃
Uronic acid	16.36〃	7.60〃	4.46〃	2.08〃
Total cellulose	61.56〃	81.46〃	82.19〃	84.30〃
α-Cellulose	60.89〃	65.32〃	63.91〃	63.25〃
β-Cellulose	17.47〃	20.56〃	21.84〃	22.48〃
γ-Cellulose	11.64〃	14.12〃	14.25〃	14.27〃
Pentosan	21.62〃	18.37〃	16.02〃	14.15〃
Copper value	1.33	1.16	0.84	0.59
Degree of polymerisation	—	1832	1688	1397

at 30°C. Intrinsic viscosities of the hemicelluloses in 10% aqueous potassium hydroxide were determined from these curves, and the degree of polymerisation was calculated by using the relation[7] $[\eta]=4.4\times10^{-3}\times(\text{D. P.})$. The component

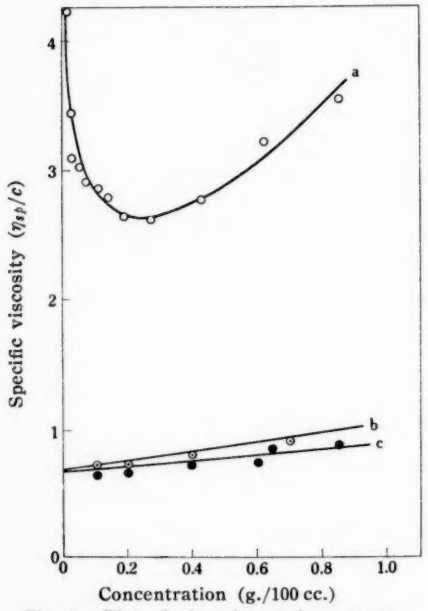

Fig. 1. Plot of viscosity against concentration for 5% extracted hemicellulose in water (a), and 5% and 16% extracted hemicellulose in 10% potassium hydroxide solution (b and c respectively).

sugars of the hemicelluloses were analysed chromatographically in the usual manner, using butanol-pyridine-water (6 : 4 : 3 by volume) as a solvent, and *o*-aminodiphenyl reagent[8] as a spraying reagent. The hemicelluloses were found to be mainly composed of D-xylose and D-glucuronic acid and of small amounts of D-mannose, D-galactose, L-arabinose and L-rhamnose. The chromatogram shows that the uronic acid is partly presented as 4-*O*-methyl-D-glucuronic acid. Data obtained are shown in Table II.

TABLE II
COMPARATIVE DATA FOR HEMICELLULOSE FRACTIONS ISOLATED FROM GANPI HOLOCELLULOSE

Fraction	Yield[a] (%)	Degree of polymerisation[b]	Uronic anhydride[c] (%)	Xylan[c] (%)
5% extract	18.0	157	15.8	80.9
16% extract	7.3	160	13.6	58.1

a) Expressed as percentage of extractive-free bast fibres and corrected for moisture and ash.
b) Calculated as a pentosan.
c) Corrected for moisture and ash.

Discussion

As is shown in Table I, substances other than cellulose are contained in the bast fibres of the Ganpi plant than in wood pulp fibres. In the paper-making processes mentioned above, these substances are still retained without much injury.

Especially, it is noticeable that much hemicellulose is kept in the fibres. The hemicellulose extracted from the bast fibres with aqueous sodium hydroxide is mainly composed of D-xylose and D-glucuronic acid (which may be partly present as 4-*O*-methyl-D-glucuronic acid),

8) T. E. Timell, C. P. J. Glaudemans and A. L. Currie, *Anal. Chem.*, **28**, 1916 (1956).

and it contains also small quantities of D-mannose, D-galactose, L-arabinose and L-rhamnose. The analytical data are interesting with regard to the fact that a polysaccharide containing D-galacturonic acid was found in the water-extract of the Ganpi bast fibres[9]. The polysaccharide is removed in the course of the preparation of holocellulose and hemicellulose. As is shown in Table II, the average degree of polymerisation of each alkali-extracted fraction of hemicellulose calculated as a pentosan is about 160. The fractions contain 15.8% and 13.6% uronic anhydride, which correspond to one carboxyl group for each six and eight pentose sugar units respectively. It is found that the hemicellulose molecule has a linear structure and the uronic groups are present along the polymer chain, because the hemicellulose indicates typical polyelectrolyte behavior in the solution. Although a great part of the uronic residue in the fibres is removed in the paper-making processes, it is found that a few percent of the uronic residue still remains in the hand-made paper.

The contents of total cellulose in the bast fibres increase naturally in each paper-making process. In the beating process, a part of α-cellulose depolymerizes to β-cellulose; this depolymerization of cellulose is also proved from the degree of polymerization. Nevertheless, the degree of polymerisation of the Ganpi cellulose is kept higher not only than wood pulp but also than Mitsumata fibres[10].

It is due to the presence of a great quantity of hemicelluloses that the long bast fibres are rendered so amenable to the wet beating process in a beater, by being fibrillated rather than cut or tangled. The hemicelluloses which are strongly hydrophilic polyuronides make also the fibres and fibrils to be more plastic, and tend to increase the areas of intimate contact between these elements, when they are felted to form a sheet of paper. Further, the hemicelluloses, cooperating with the plant mucilage employed, cause the fibres to be well dispersed in water to accomplish a good distribution of fibres in the fibre mat. Both these effects of the hemicelluloses increase the strength, transparency, density, softness and grease-proofness of the paper produced. This view would be proved, for example, by Leech's experiment[11] in which locust bean gum was employed in the beating of wood pulp for the sake of increasing the strength of the paper made from the pulp. But Jayme[12] assents that the quality as well as quantity of hemicellulose present in the fibres is of importance in attaining strength in paper made from pulp. Limeric and Corey[13] said that the hemicellulose containing many uronic acids is of advantage for the production of strong papers. The hemicellulose molecule of Ganpi bast fibres has comparatively long linear structure, and is strongly hydrophilic on account of the presence of uronic acid residue along the molecular chain. This fact has probably a significant bearing on the character of Japanese hand-made paper. It is considered to be necessary to investigate the question further to find a complete picture of the chemical nature of Ganpi hemicellulose.

Summary

The composition of the bast fibres of Ganpi plant (*Wickstroemia sikokiana* Franch. et Sav.) was investigated in the processes of the traditional paper-making of Japan. It was found that hemicelluloses of the bast fibres had significant bearings on the paper-making and the excellent character of Japanese paper.

The hemicellulose isolated from holocellulose of the Ganpi bast fibres by alkaline extraction were found to be composed of 13.6~15.8% of D-glucuronic acid (which is partly present as 4-*O*-methyl-D-glucuronic acid), 58.1~80.9% of D-xylose, and small amounts of D-mannose, D-galactose, L-arabinose, and L-rhamnose. It was shown that the degree of polymerisation of the hemicellulose calculated as a pentosan is about 160, and the molecule has basically a linear structure in which the uronic groups are present along the polymer chain at a ratio of one carboxyl group for each six or eight pentose sugar units.

The authors wish to thank Mr. M. Inano for help in the analysis of component sugars and uronic acid.

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13) J. M. Limeric and A. J. Corey, *Pulp Paper Mag. Canada*, **47**, No. 4. 62 (1946).

Synthesis of 2-Alkyl-4H, 1, 3-benzoxazine-4-ones

By Takeyosi HANADA

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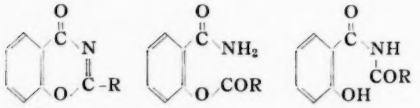
4*H*,1,3-Benzoxazine-4-one derivatives are expected to show interesting chemical and biological properties, owing to the characteristic structure that the carbonyl group adjacent to N=C double bond is present in them. However, only a few 2-aryl derivatives have been reported[1,2], and no literature has appeared concerning 2-alkyl derivative. Titherley[1] reported the preparation of 2-phenyl-4*H*,1,3-benzoxazine-4-one (I: R=Ph) from *O*- or *N*-benzoylsalicylamide by the action of hydrogen chloride in boiling xylene. But Titherley et al.[3] failed in the preparation of 2-methylbenzoxazinone (Ia) from *O*-acetylsalicylamide (IIa) by the same procedure, and isolated only *N*-acetylsalicylamide (IIIa) produced by O→N acyl rearrangement. They assumed that the abortive isolation of 2-methylbenzoxazinone was due to its decomposition by alkali which was present.



I II III

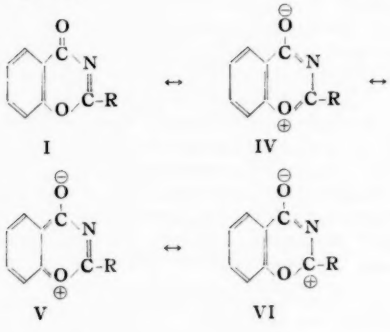
(a: R=CH_3, b: R=C_2H_5, c: R=C_3H_7)

In the present experiment *O*-acetylsalicylamide (IIa) was treated with hydrogen chloride in boiling xylene according to the procedure of Titherley[1], and without using alkali there were isolated yellow crystals, $C_9H_7O_2N$, m. p. 217°C, together with *N*-acetylsalicylamide (IIIa) produced by the acyl rearrangement. The yellow compound was considered to be 2-methyl-4*H*,1,3-benzoxazine-4-one (Ia). Its infrared spectrum showed carbonyl band at 1680 cm^{-1}, and C=N band at 1645 cm^{-1}, and indicated also the absence of both OH and NH group. This was insoluble in cold dilute aqueous alkali and showed no coloration with ferric chloride in chloroform. It also was produced from *N*-acetylsalicylamide (IIIa) in low yield under similar conditions.

Similarly, 2-ethyl- and 2-propyl-benzoxazinone (Ib and Ic) were synthesized from *O*-propionyl- and *O*-butyrylsalicylamide (IIb and IIc) respectively, though in poor yield. Their chemical and physical properties were very similar to those of the 2-methyl compound. It is noticeable that the infrared spectra of these compounds are essentially identical in the region below 7μ, while the 2-phenyl homologue shows an infrared band of carbonyl group at 1665 cm^{-1} and of C=N group at 1645 cm^{-1}.

2-Methyl-4*H*, 1, 3-benzoxazine-4-one was stable towards acid in contrast with the 2-phenyl homologue, but very sensitive to alkali; it was easily hydrolyzed to salicylamide by boiling with 1 N-sodium hydroxide for a few minutes. When heated with dilute aqueous ammonia it produced an alkali-soluble compound, m. p. 227°C (empirical formula, $C_{18}H_{15}O_3N_3$), of which the structure is now under investigation.

2-Alkyl-benzoxazinone contains a characteristic skeleton, —CO—N=C—, which has not yet been studied well and is assumed to be stabilized by a hydrid among the structures I, IV, V, and VI. It is supposed that the carbon atom at the 2-position is easily attacked by the nucleophilic reagent owing to the influence of the carbonyl group.



I ↔ IV ↔

V ↔ VI

1) A. W. Titherley, *J. Chem. Soc.*, **97**, 200 (1910).
2) A. Mustafa and A. E. A. A. Hassan, *J. Am. Chem. Soc.*, **79**, 3846 (1957).
3) A. W. Titherley and W. L. Hicks, *J. Chem. Soc.*, **99**, 866 (1911).

Experimentral

***O*-Acetylsalicylamide (IIa).**—McConnan and Titherley[4] prepared this compound by the action of acetyl chloride on salicylamide in pyridine at −15°C. In the present study it was obtained by the following procedure: a few drops of concentrated sulfuric acid were added to a mixture of 20 g. of salicylamide and 50 ml. of acetic anhydride. After this mixture was kept for about 10 min., 500 ml. of water was added in order to decompose the excess of acetic anhydride. Upon filtration and washing with water, 18.5 g. (71%) of crude product was obtained and used for the next step without further purification. Recrystallization from ethyl acetate gave colorless needles, m. p. 138°C (Reported m. p. 138°C.).

***O*-Propionylsalicylamide (IIb).**— A solution of 10 g. of salicylamide in 20 ml. of pyridine was cooled to −15°C and 6.8 g. of propionyl chloride was added dropwise under vigorous stirring. After the addition, the mixture was kept for 30 min. at the same temperature, and 100 ml. of ether was added under stirring and then the ether was decanted off. To the remaining pasty mixture was added 1 N-sulfuric acid at 0°C, under stirring, in the course of ca. 10 min. The solid was filtered and washed with water. After the above ethereal solution had been allowed to stand for several hours, an additional small quantity of crystals was separated. The combined solids (9.1g.; 65%) were recrystallized from benzene to give colorless needles, m. p. 112∼113°C, which showed no coloration with ethanolic ferric chloride.

Anal. Found: C, 62.27; H, 5.93. Calcd. for $C_{10}H_{11}O_3N$: C, 62.16; H, 5.74%.

***N*-Propionylsalicylamide (IIIb).**—When dilute aqueous ammonia was added to IIa, the solid was dissolved gradually and a yellow solution was obtained. By acidification with dilute hydrochloric acid colorless crystals were obtained, m. p. 123∼125°C. Recrystallization from benzene gave colorless needles, m. p. 126∼127°C, readily soluble in ethanol and ether; they revealed a purple-brown color with ethanolic ferric chloride.

IIIb was also obtained by boiling IIb with water for 30 min.

Anal. Found: C, 62.68; H, 5.92. Calcd. for $C_{10}H_{11}O_3N$: C, 62.16; H, 5.74%.

***O*-Butyrylsalicylamide (IIc).**—To a solution of 10 g. of salicylamide in 20 ml. of pyridine, was added 7.8 g. of butyryl chloride at −15°C following the same procedure as in the case of IIb. A solid thus obtained was crystallized from benzene to yield colorless needles, but the melting point was not sharp (m. p. ca. 90∼110°C) because of persistent contamination of IIIc.

Anal. Found: C, 64.02; H, 6.59. Calcd. for $C_{11}H_{13}O_3N$: C, 63.75; H, 6.32%.

***N*-Butyrylsalicylamide (IIIc),**—This material was prepared by the action of dilute aqueous ammonia on IIc, or by boiling IIc with water for 20 min. Recrystallization from benzene gave colorless needles, m. p. 128∼129°C, readily soluble in ethanol and ether. They produced an orange brown color with ethanolic ferric chloride.

Anal. Found: C, 63.64; H. 6.55. Calcd. for $C_{11}H_{13}O_3N$: C, 63.75; H, 6.32%.

2-Methyl-4*H*, 1, 3-benzoxazine-4-one (Ia).—a) *From O-Acetylsalicylamide (IIa).*—A mixture of 15 g. of IIa and 200 ml. of xylene was heated in a bath to 145°C, and when the solution became clear, a stream of dry hydrogen chloride was passed through for several min. By gradually raising the temperature of the bath to 155°C, the xylene was allowed to distil out, carrying with it the water formed during the reaction. In order to make up for the loss of hydrogen chloride by distillation, a few bubbles of the gas were passed into the solution at an interval of several minutes. When the greater part of the solvent was distilled off, the residue solidified on cooling. It was treated with warm ethanol to remove IIIa. The remaining yellow solid (7.4g.; 50%) was repeatedly crystallized from benzene to yield yellow needles (Ia), m. p. 217°C. It was insoluble in ethanol and ether, soluble in dioxane, pyridine and chloroform. The infrared spectrum showed bands at 1684 cm^{-1} (C=O) and 1645 cm^{-1} (C=N).

Anal. Found: C, 67.05; H, 4.18; N, 8.74. Calcd. for $C_9H_7O_2N$: C, 67.06; H, 4.35; N, 8.69%.

From the ethanolic solution, by evaporation of the solvent and recrystallization from benzene, colorless needles, m. p. 140∼141°C, were obtained. The melting point was not depressed on admixture with IIIa.

b) *From N-Acetylsalicylamide (IIIa).*—A solution of 6.5 g. of IIIa in 25 ml. of dry xylene was heated for ca. 5 hr. under passage of dry hydrogen chloride. After removal of the greater part of the solvent under reduced pressure, yellow crystals deposited on cooling. After recrystallization from benzene, the compound had m. p. 217°C; mixed m. p. with Ia prepared from IIa, 217°C.

2-Ethyl-4*H*, 1, 3,-benzoxazine-4-one (Ib).—A solution of 15 g. of IIb in 200 ml. of dry xylene or toluene was heated in the presence of dry hydrogen chloride following the same procedure as above. The product, after removal of the ethanol-soluble part, was crystallized from benzene to yield yellow needles m. p. 212∼213°C, insoluble in ethanol and ether. The infrared spectrum showed bands at 1680 cm^{-1} (C=O) and 1645 cm^{-1} (C=N).

Anal. Found: C, 68.48; H, 5.40; N, 8.23. Calcd. for $C_{10}H_9O_2N$: C, 68.56; H, 5.18; N, 8.00%.

The ethanol extracts obtained above were concentrated to a solid, which on crystallization from benzene gave colorless needles, m. p. 126∼127°C, undepressed on admixture with IIIb.

2-Propyl-4*H*, 1, 3-benzoxazine-4-one (Ic).—A solution of 15 g. of IIc in 180 ml. of toluene was heated with dry hydrogen chloride in the same manner as described above. In this case, the residue was wholly soluble in ethanol, but on standing overnight, a small quantity of crystals separated out from the ethanol solution. Recrystallization from benzene gave yellow plates, m.p. 142∼143.5°C, soluble in ethanol and benzene.

4) J. McConnan and A. W. Titherley, *J. Chem., Soc.*, **89**, 1333 (1906).

The infrared spectrum showed bands at 1680 cm^{-1} (C=O) and 1645 cm^{-1} (C=N).

Anal. Found: C, 69.77; H, 6.06. Calcd. for $C_{11}H_{11}O_2N$: C, 69.82; H, 5.86%.

Further concentration of ethanolic mother liquor gave crystals which on repeated recrystallizations from benzene had m. p. 124~128°C. The material did not depress the melting point of an authentic sample of IIIc.

Alkaline Hydrolysis of Ia. — When Ia was boiled for a few minutes with 1 N sodium hydroxide, a pale yellow solution was formed. After acidification with diluted hydrochloric acid, the precipitates formed were collected and recrystallized from water to give colorless needles, m. p. 136~137°C. The material was identified as salicylamide on the basis of the mixed melting-point test.

Reaction of Ia with Aqueous Ammonia. — A mixture of 2 g. of Ia, 60 ml. of 3N aqueous ammonia and 60 ml. of ethanol was heated for 30 min. on a steam bath. After cooling the yellow solution was acidified with dilute hydrochloric acid, and the precipitates were collected and recrystallized twice from benzene (once using charcoal) to give colorless needles, m. p. 227°C, in almost quantitative yield. The material was soluble in ether, ethanol and chloroform, and showed no color with ferric chloride in ethanol. It was dissolved in dilute sodium hydroxide solution to give a yellow solution, and was recoverable, as it was, from this solution, after ten minutes' heating in a water bath.

Anal. Found: C, 67.55; H, 4.31; N, 13.09; Mol. wt. (Rast), 323. Calcd. for $C_{18}H_{15}O_3N_3$: C, 67.28; H, 4.71; N, 13.08%; mol. wt., 321.

The infrared spectrum showed bands at 3390 cm^{-1} (OH) and 1640 cm^{-1} (C=O).

Summary

2-Alkyl-4*H*,1,3-benzoxazine-4-ones (Ia, Ib, and Ic) were synthesized from the corresponding *O*-acylsalicylamides (II), and some of the properties of I were studied.

The author wishes to thank Professor T. Irie for his kind guidance and encouragement throughout this work. He is also indebted to Miss N. Fujino for the microanalyses.

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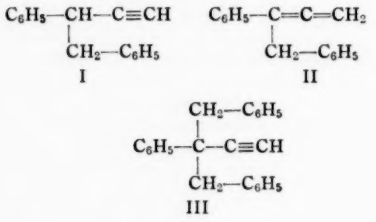
Benzylation of Allylbenzene. Formation of 3,4-Diphenyl-1-butene and 3-Benzyl-3,4-diphenyl-1-butene

By Teisuke ANDO and Niichiro TOKURA

(Received July 2, 1958)

In the preceding papers[1,2] the authors reported the formation of 3,4-diphenyl-1-butyne (I), 3,4-diphenyl-1,2-butadiene (II), and 3-benzyl-3,4-diphenyl-1-butyne (III) by the reaction of benzyl chloride and sodium acetylide in liquid ammonia.



I II

III

It is assumed that 3-phenyl-1-propyne (i.e. propargylbenzene) (IV) is formed as an intermediate at the first stage.

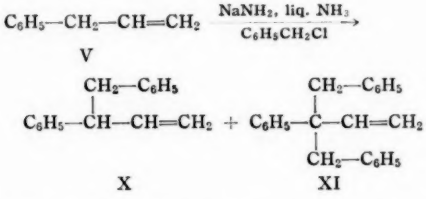
IV V

In 1952, Young, Kosmin, Mixer and Campbell[3] reported on methylation and allylation of allylbenzene (V) in liquid ammonia. More recently, Mixer and Young[4] conducted the same reactions in *n*-pentane. Herbrandson and Mooney[5] reported the isomeric transformation

1) T. Ando and N. Tokura, This Bulletin, **30**, 259 (1957).
2) T. Ando and N. Tokura, ibid., **31**, 351 (1958).
3) W. G. Young, M. Kosmin, R. Y. Mixer and T. W. Campbell, *J. Am. Chem. Soc.*, **74**, 608 (1952).
4) R. Y. Mixer and W. G. Young, ibid., **78**, 3379 (1956).
5) H. F. Herbrandson and D. S. Mooney, ibid., **79**, 5809 (1957).
6) W. v. Miller and G. Rohde, *Ber.*, **25**, 2015 (1892).

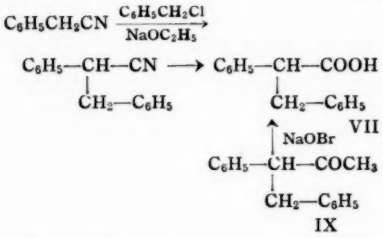
between allylbenzene and propenylbenzene in the presence of butyllithium or lithium amide.

Since allylbenzene (i.e. 3-phenyl-1-propene) (V) is closely related to IV in its structure, it was also expected that the benzylation of V in liquid ammonia would afford mono- and di-benzyl derivatives of V, corresponding to I and III in the benzylation of acetylene. The present paper, records the results of the study on the benzylation reaction which was observed to occur as expected. The structures of the products formed in this reaction and the relations among the products from benzylation of allylbenzene, benzyl cyanide and acetylene have been established unequivocally.



When V was allowed to react with an equi-molecular amount of benzyl chloride in the presence of sodium amide in liquid ammonia, two fractions were obtained, A, b. p. 160~162°C (17 mm.), and B, b. p. 191~192°C(2 mm.).

By oxidizing A with potassium permanganate, a white crystalline substance (VI), m. p. 88~89°C, was obtained. Miller and Rohde[6] reported on the synthesis of 2,3-diphenylpropionic acid (VII), and it was observed that the substance exists in three isomers, m. p. 82°C, and 95~96°C[7,8]; the present authors prepared 2,3-diphenylpropionic acid (VII) by hydrolyzing 2,3-diphenylpropionitrile (VIII), obtained by the reaction of benzyl cyanide with an equi-molecular amount of benzyl chloride in the presence of sodium alcoholate according to the method of Miller and Rohde[6].



In this case two kinds of crystalline product having melting points 82°C and 88~89°C, respectively, were isolated, but the one having the highest melting point, 95~96°C, was not isolated. A mixture of the crystalline product having m. p. 88~89°C and VI gave no lowering of the melting point. By oxidizing the known compound, 3,4-diphenyl-2-butanone[9] (IX), with sodium hypobromite, an acid showing an m. p. and a mixed m. p. with VI of 88~89°C was also obtained.

Infrared spectra in potassium bromide disks and carbontetrachloride solution of two specimens of 2,3-diphenylpropionic acid having m. p. 82~82.5°C and 88~89°C were measured. The spectra in the disks gave different curves, while those in the solution gave the same. (Compare Fig. 1 and the experimental part.).

Thus, the structure of VI being established as 2,3-diphenylpropionic acid, A is regarded as 3,4-diphenyl-1-butene (X), which is further supported by the elementary analysis (molecular formula: $C_{16}H_{16}$), and infrared spectrum.

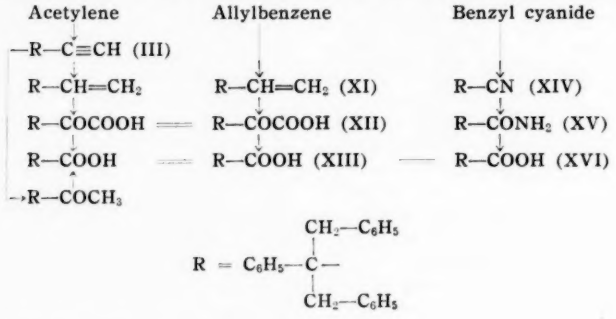
The boiling point, the molecular formula $C_{23}H_{22}$ and the infrared spectrum of B were almost coincident with those of the partially hydrogenated product of III, 3-benzyl-3,4-diphenyl-1-butene (XI). The structure of XI for B was proved by several reactions as follows. Oxidation of B with potassium permanganate afforded an α-keto acid (XII), m. p. 138.5~139.5°C, which showed no depression of the mixed melting point with an authentic phenyldibenzylpyruvic acid[2]. Furthermore, oxidation of XII with potassium permanganate or hydrogen peroxide gave an acid (XIII), m. p. 122~123°C, a mixture of which with the α-form of 2-benzyl-2,3-diphenylpropionic acid[2] obtained previously gave no melting point lowering. As was already reported[2], this acid showed a polymorphic transformation and the melting point was raised to 153~154°C after standing for two months.

No material to be considered as derived from propenylbenzene was isolated in this reaction. Therefore, in the metallation of allylbenzene(V) with sodium amide in liquid ammonia, the carbon atom adjacent

7) C. R. Hauser and W. J. Chambers, *J. Am. Chem. Soc.*, **78**, 4942 (1956).
8) N. Campbell and E. Ciganck, *J. Chem. Soc.*, **1956**, 3834.
9) M. M. Tiffeneau and M. J. Levy, *Bull. soc. chim. France*, **33**, 779 (1923).

TABLE I

BENZYLATION OF ACETYLENE, ALLYLBENZENE, AND BENZYL CYANIDE



to the benzene ring was metallated, and the action of benzyl chloride afforded the mono- or di-benzyl compounds, 3, 4-diphenyl-1-butene (X) (40 percent) and 3-benzyl-3, 4-diphenyl-1-butene (XI) (30 percent).

Benzylation of allylbenzene, benzyl cyanide and acetylene[1,2], and the relations of the products are schematically represented by Table I.

Experimental[10]

Benzylation of allylbenzene.—Liquid ammonia (700 cc.) was taken in a three-necked flask of 100 cc. capacity equipped with a mechanical agitator, a dry-ice condenser and a dropping funnel, and kept at $-50°\pm5°$C in a dry-ice-ethanol bath, and 14 g. of metallic sodium was dissolved in the liquid ammonia. After being mixed with a minute amount of ferric nitrate, the content was agitated for about 20 minutes to produce sodium amide. After another 20 minutes' agitation, 60 g. of allylbenzene (b. p. 47°C/12 mm.) was added in 30 minutes. The solution was tinged with reddish brown color. It was further agitated for 20 minutes and 68 g. of benzyl chloride was added drop by drop in 40 minutes. When the addition of the same mole of benzyl chloride was completed, the color of the solution changed to grayish white. The benzylation reaction was exothermic. The dry-ice bath was removed and the flask was left overnight at room temperature, while liquid ammonia was naturally evaporated off. The residue was extracted with ether, and the ethereal solution was washed with water to neutral reaction and dried with dehydrated Glauber's salt. After the ether was distilled off, the residue was fractionated in vacuo to give two fractions: A fraction, boiling at 150～155°C/11 mm., (yield 44.2 g.), which was redistilled to give 38.7 g. of b. p. 160～162°C/17 mm. B fraction, boiling at 175～200°C/2 mm., (yield 24.6 g.), which gave 18.2 g. of b. p. 191～192°C/2 mm. by redistillation.

10) Melting points and boiling points were not corrected.

	Molecular formula	Crude (g.)	Distillate (%)	Theoretical yield based on benzyl chloride (%)
A	$C_{16}H_{16}$	44.2	51	40
B	$C_{23}H_{22}$	24.6	28	30

Anal. Found: C, 92.32; H, 7.77. Calcd. for A or $C_{16}H_{16}$: C, 92.26; H, 7.74%. I. R. ν_{max}: 1635, 1452, 1415, 990, and 910 cm^{-1}. *Anal.* Found: C, 92.61; H, 7.39. Calcd. for B or $C_{23}H_{22}$: C, 92.57; H, 7.43%. I. R. ν_{max}: 1634, 1455, 1415, 1005, and 912 cm^{-1}.

Oxidation of A with potassium permanganate. 2, 3-Diphenylpropionic acid (VI).—A (4.1 g.) was dissolved in 300 cc. of acetone in a three-necked flask of 1000 cc. capacity equipped with an agitator. Powdered potassium permanganate (9 g.) was added to the solution little by little with agitation at the room temperature. After 6 hours' agitation, the mixture was left overnight at room temperature, and then the solvent was distilled off. Water was added to the residue and manganese dioxide was dissolved by passing sulfur dioxide gas into the mixture.

The substance in crystalline suspension was extracted with ether and the ethereal solution was washed with aqueous alkali. The aqueous solution was acidified and extracted with ether. The ethereal solution was washed with water until the solution became neutral. After drying with dehydrated Glauber's salt, the solution was evaporated to give 4 g. (88 %) of a white crystalline substance, m. p. 70～83°C, and recrystallization from petroleum ether (b. p. 60～80°C) gave VI, m. p. 88～89°C. A mixture of VI and 2, 3-diphenylpropionic acid (VII), m. p. 88～89°C, prepared by the method given by Miller and Rohde[6], gave no melting point lowering.

Anal. Found: C, 79.81; H, 6.30. Calcd. for 2, 3-diphenylpropionic acid (VI) or $C_{15}H_{14}O_2$: C, 79.62; H, 6.24%.

2, 3-Diphenylpropionic acid (VII)[6].—Metallic sodium (12 g.) was dissolved in 100 g. of absolute ethanol in a flask of 300 cc. capacity, and 58 g. of benzyl cyanide and 69 g. of benzyl chloride were added and the mixture was refluxed for 4 hours. Sodium chloride was filtered off and

the solution was evaporated. Vacuum distillation of the residue gave 33 g. (48%) of unchanged benzyl cyanide and 10 g. (15.7%) of diphenylpropionitrile, m. p. 57.5~58.5°C (recrystallized from alcohol). The nitrile (1 g.) was heated with 2 cc. of concentrated hydrochloric acid in a sealed tube at 130°C for 5 hours. After the reaction was completed, the product was made alkaline and the unchanged nitrile and the intermediate acid amide were removed with ether. The remaining aqueous solution was acidified and extracted with ether. The crystalline substance from the ethereal solution was recrystallized from petroleum ether (b. p. 60~80°C). Needles, m. p. 82~82.5°C. Recrystallization of the needles from water gave small white plates, m. p. 88~89°C. Melting points of the two crystalline specimens were coincident with those of 2,3-diphenylpropionic acid. 82°C and 88~89°C, given in the literature[6]).

Anal. Found: C, 86.75; H, 6.43; N, 6.67. Calcd. for 2,3-diphenylpropionitrile (VIII) or $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.76%. Found: C, 79.74; H, 6.73; N, 6.06. Calcd. for 2,3-diphenylpropionamide or $C_{15}H_{15}ON$: C, 79.97; H, 6.71; N, 6.22%. Found: C, 79.56; H, 6.22. Calcd. for 2,3-diphenylpropionic acid (VII) or $C_{15}H_{14}O_2$: C, 79.62; H, 6.24%.

Crystals having m. p. 82~82.5°C: I. R. crys. ν_{max}: 3300~2300, 1700, 1688, and 940 cm^{-1}, I. R. CCl_4 soln. ν_{max}: 3300~2300 and 1708 cm^{-1}, U. V. λ_{max}: 258 mμ (log ε: 2.76) and 265 mμ (log ε: 2.65).

Crystals having m. p. 88~89°C: I. R. crys. ν_{max}: 3180, 1724, 1677, and 1173 cm^{-1}, I. R. CCl_4 soln. ν_{max}: 3300~2400, and 1705 cm^{-1}, U. V. λ_{max}: 258 mμ (log ε: 2.68), and 265 mμ (log ε: 2.61).

Synthesis and oxidation of 3,4-diphenylbutanone (IX). — According to Tiffeneau and Lévy[9]), phenylacetone was metallated with sodium alcoholate and then refluxed with the same mole of benzyl chloride for 2 hours. The product boiled at 188~189°C/20 mm. and melted at 31~32°C after recrystallization from petroleum ether (b. p. 40°C). The same m. p. was given by the literature[9]). Its oxime, m. p. 138~138.5°C. (literature[9]): 134~135°C) semicarbazone, m.p. 169~170°C. (literature[9]): 168°C).

Anal. Found: C, 85.77; H, 6.94. Calcd. for 3,4-diphenyl-2-butanone (IX) or $C_{16}H_{16}O$: C, 85.68; H, 6.84%. I. R. oil ν_{max}: 1700, 1351, 1148, 1088, and 1030 cm^{-1}, U. V. λ_{max}: 268 mμ (log ε: 2.78), 265 mμ (log ε: 2.74) and 288 mμ (log ε: 2.70).

Sodium hypobromite[11]) was prepared by adding 5 cc. of bromine to an aqueous solution of 15 g. of sodium hydroxide in 50 cc. water cooled in ice. It was added to a solution of 5 g. of the above substance of m. p. 31~32°C in 50 cc. of 1,4-dioxane with vigorous agitation and the mixture was kept at the room temperature for 2 days. On concentration, the aqueous layer gave a grayish-white semi-solid, from which the unchanged substance was removed with ether. After acidifying with hydrochloric acid, the product was extracted with ether. The ethereal solution gave 1.8 g. (36.4%) of a crystalline substance, m. p. 82~82.5°C. Recrystallization from petroleum ether (b. p. 60~80°C) gave white crystals, m. p. 88~89°C. A mixture of the acid and VI showed no lowering of the melting point.

Oxidation of B with potassium permanganate. — *Phenyldibenzylpyruvic acid (XII).* — B (4.2 g.) was dissolved in 400 cc. of acetone in a three-necked flask of 2 liter capacity equipped with an airtight agitator and a reflux condenser. To the solution 8 g. of potassium permanganate dissolved in 400 cc. of water was added and the mixture was agitated for 48 hours at the room temperature. After removal of acetone, sulfur dioxide gas was introduced into the residue under cooling in ice and then the solution was made alkaline with dilute aqueous caustic soda. The unchanged neutral part was extracted with ether and the remaining alkaline layer was acidified with hydrochloric acid and extracted with ether. The ethereal solution gave 4.3 g. of a crystalline substance, m. p. 138~139.5°C, in a yield of 88%. The melting point of the keto acid (XII) did not change on admixture with phenylbenzylpyruvic acid obtained by oxidation of III.

Anal. Found: C, 79.92; H, 5.98. Calcd. for phenyldibenzylpyruvic acid (XII) or $C_{23}H_{20}O_3$: C, 80.21; H, 5.85%. I. R. ν_{max}: 1722, 1711, and 1370 cm^{-1}.

The α-form of 2-benzyl-2,3-diphenylpropionic acid (XIII). — *a) Oxidation of XII with potassium permanganate.* — XII (0.5 g.) was dissolved in 100 cc. of 2% aqueous sodium hydroxide in a round-bottom flask of 300 cc. capacity, and to the solution 50 cc. of 1% aqueous potassium permanganate was added. The mixture was agitated for 8 hours and left to stand overnight. It was then neutralized with dilute sulfuric acid, treated with sulfur dioxide gas to dissolve manganese dioxide, and extracted with ether. The white crystalline substance from the ethereal solution was recrystallized from ligroin (b. p. 80~100°C). White scales m. p. 121~122°C. (α-form) (XIII). Yield 0.2 g. (43.5%).

b) Reaction of XII with hydrogen peroxide. — In a beaker of 200 cc. capacity, 1.5 g. of XII was mixed with 20 cc. of 10% sodium hydroxide and 30 cc. of 10% sodium hydrogen peroxide and the mixture was allowed to stand overnight in an ice box. Then 10 cc. more of hydrogen peroxide was added to the mixture with agitation. After 8 hours, the mixture was acidified and extracted with ether. The ethereal solution gave 0.4 g. (87%) of fine scales, m. p. 118~120°C, and recrystallized from ligroin (b. p. 80~100°C). White scales (α-form, XIII), m. p. 122~123°C. Yield 3 g. No melting point depression was observed on admixture of the acid (XIII) with α-form of 2-benzyl-2,3-diphenylpropionic acid, obtained by the oxidation of III.

Anal. Found: C, 83.32; H, 6.42. Calcd. for 2-benzyl-2,3-diphenylpropionic acid (XIII) or

11) W. S. Johnson, C. D. Gutsche and R. D. Offenhauer, *J. Am. Chem. Soc.*, **68**, 1648 (1946).

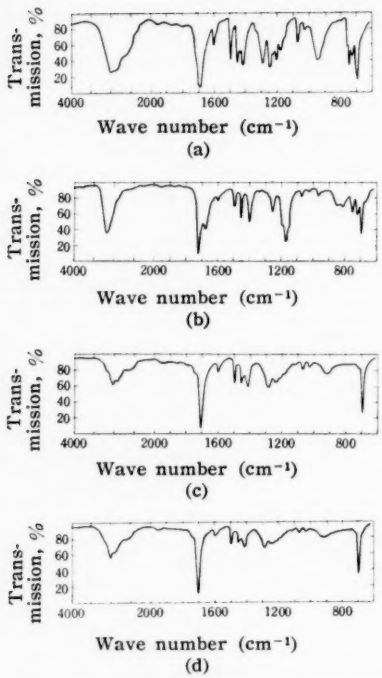


Fig. 1.
(a) KBr disk of the specimen of 2, 3-diphenylpropionic acid melting at 82°C.
(b) KBr disk of specimen of the same compound melting at 88~89°C.
(c) A CCl_4 solution of the specimen of the same compound melting at 82°C.
(d) A CCl_4 solution of the specimen of the same compound melting at 88~89°C.

$C_{22}H_{20}O_2$: C, 83.51; H, 6.37%. I. R. crys. ν_{max}: 3200~2300, and 1702 cm^{-1} I. R. CCl_4 soln. ν_{max}: 3300~2400 and 1700 cm^{-1} U. V. λ_{max}: 258 mμ (log ε: 2.67) and 265 mμ (log ε: 2.56).

On standing for about two months at room temperature, the α-form of XIII, m. p. 122~123°C, was changed to the β-form, m. p. 153~154°C. In I. R. and U. V. spectra of the two forms, not even a slight difference was estimated. A mixture of the β-form, m. p. 153~154°C, and the β-form of 2-benzyl-2, 3-diphenylpropionic acid (XVI), synthesized by the method of Hauser and Brasen[12], gave no melting point lowering.

12) C. R. Hauser and W. R. Brasen, ibid., **78**, 494 (1956).
13) R. H. Baker, ibid., **70**, 3857 (1948).

Benzylation of benzyl cyanide. The β-form of 2-benzyl-2, 3-diphenylpropionic acid (XVI).—According to the method of Hauser et al.[12] and Baker[13], 2-benzyl-2, 3-diphenylpropionitrile (XIV) was obtained in a fairly good yield. The product (XIV), m. p. 81~83°C, b. p. 204~205°C/2 mm., was refluxed with 70% sulfuric acid in glacial acetic acid for 4 days, and gave 2-benzyl-2, 3-diphenylpropionamide (XV), m. p. 122.7~124°C. (Baker[11]: m. p. 111~112°C).

Anal. Found: N, 4.20. Calcd. for 2-benzyl-2, 3-diphenylpropionamide (XV) or $C_{22}H_{21}ON$, 4.44%.

Treatment of the amide (XV) with sodium nitrite gave 2-benzyl-2, 3-diphenylpropionic acid (XVI, β-form). The melting point of the substance and of a mixture with an authentic specimen of the β-form was the same, m. p. 154~154.5°C.

Anal. Found: C, 83.51; H, 6.45. Calcd. for 2-benzyl-2, 3-diphenylpropionic acid (XVI) or $C_{22}H_{20}O_2$: C, 83.51; H, 6.37%. I. R. ν_{max}: 5300~2200 and 1700 cm^{-1}, U. V. λ_{max}: 258 mμ (log ε: 2.67) and 265 mμ (log ε: 2.56).

Summary

When allylbenzene was treated with the same moles of sodium amide and benzyl chloride in liquid ammonia, one or two benzyl radicals were introduced into allylbenzene to produce 3, 4-diphenyl-1-butene and 3-benzyl-1-butene.

The reaction is similar to the well-known reaction[12] of benzyl cyanide and benzyl chloride in liquid ammonia and that[13] of 2-phenyl-1-ethanol and benzyl chloride in benzene.

Two forms of 2, 3-diphenylpropionic acid were isolated and their I. R. spectra were measured. Different curves were obtained in KBr disks, while the identical curves were obtained carbon tetrachloride solution.

Infrared absorption spectra were measured by Professor Kinumaki and his associates of this Institute and the elementary analyses were performed in the laboratory of Shionogi and Company, Ltd., to whom the writers are deeply indebted.

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Thermal Effects of Some Kaolin Minerals. I. Kaolinite and Kibushi-clay

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All kaolin minerals are made of aluminosilicate layers in their crystal structures. However, there are imperfections in the mode of stacking of unit layers, and this leads to variety in the structure of kaolin minerals[1]. The different properties which are found among kaolin minerals are due to there being many kinds of characteristic factor in each mineral. Of such factors, the most important one is the structural perfection or imperfection, that is, the degree of crystallinity including the stacking disorder.

It is well known that a kaolinite transforms into mullite through heat-treatment at 950~1000°C[2]. Investigations on the structural change of kaolin minerals with heat-treatment have been made chiefly in a temperature region higher than 950°C. However, little investigation has been done in regard to the effect of heat-treatment in the relatively low temperature region.

The course of the transformation of a kaolinite into mullite involves two major structural changes. One is a structural change due to the loss of the adsorbed water. The other is a structural change caused by the loss of the lattice water. In this paper, the fundamental information regarding the change in the structure of kaolinite with heat-treatment, in the relatively low temperature region, are presented, through X-ray diffraction method, differential thermal analysis and particularly using these together with density measurement.

Experimental

Twenty samples of kaolinte and kaolin mineral of fireclay type were used in this study. In studying these samples continuous disordering was observed among different samples. For the structural changes of kaolinite and kaolin mineral of fireclay type through heat-treatment, the structural changes of the following three samples are generally representative of the whole. Three of the samples mentioned above are as follows; Kaolinite from Mesa Alta, N.M., U.S.A.; Kaolinite from Drybranch, Geor., U.S.A.; Kibushi-clay from Shidare, Gifu, Japan. Two of the kaolinite samples are the API Standard Clay Minerals; Kibushi-clay is a kaolin mineral of fireclay type. The structural characteristics of these samples have been discussed in the previous paper[3]. The original samples were powdered and sieved through 250 mesh. The heat-treatment was made in an electric furnace under the ordinary atmosphere, keeping at a given temperature for an hour.

The X-ray powder diagrams were recorded by the X-ray diffractometer (Geigerflex). Experimental conditions were as follows. Filtered Copper radiation (Cu$K\alpha$:1.5418 Å) at about 35 kV and 15 mA was used; scanning speed was 1° or 1/4° 2θ per minute; time constant was 4 seconds; receiving slit was 0.2 mm or 0.1 mm; angular aperture was 1° or 1/2°.

The differential thermal analysis curves were obtained by the apparatus described by Sudo et al.[4]. Care was taken to pack a specimen into the sample block in the homogeneous manner and also to keep the weight of the specimen constant. The mean heating rate is 12.5°C per minute.

The density of the specimens was measured by a pycnometer in carbon tetrachloride. It was made in the original state after it had been dried at 110°C in order to avoid the effect of the adsorbed or interlayer water.

Results and Discussion

X-ray Diffraction Studies.—X-ray diffractometer traces for heat-treated kaolinite and Kibushi-clay are given in Figs. 1 and 2, respectively.

In the traces of Mesa Alta kaolinite, which are observed in the X-ray diagram before it is heat-treated at 400°C, an increase in the intensity of reflection, particularly (00 l), and the reduction in the line breadth are most remarkable. In the 545°C heat-treated specimen, the intensity of all reflections, particularly (00 l) reflections, sharply decreases. In this specimen,

1) G.W. Brindley and K. Robinson, *Trans, Farad. Soc.*, **42B**, 198 (1946).
2) W. F. Bradley and R. E. Grim, *Am. Mineral.*, **36**, 182 (1951).
W. D. Jones, *Min, Mag.*, **30**, 186 (1953).
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3) H. Takahashi, This Bulletin, **31**, 275 (1958).
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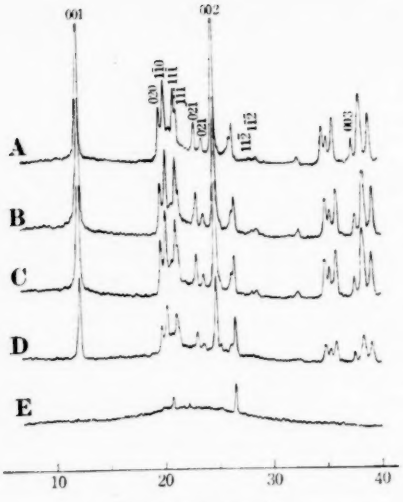

Fig. 1. X-ray diffractometer traces of heat-treated specimens of kaolinite (Mesa Alta, N.M.).
A, original kaolinite
B, treated at 200°C
C, treated at 400°C
D, treated at 545°C
E, treated at 700°C

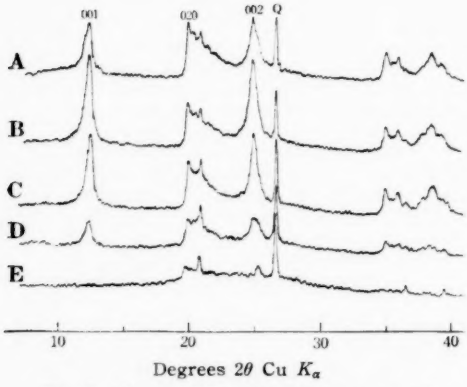

Fig. 2. X-ray diffractometer traces of heat-treated specimens of Kibushi-clay.
A, original clay
B, treated at 200°C
C, treated at 400°C
D, treated at 545°C
E, treated at 700°C

the $(11\bar{2})$ reflection of 3.14 Å spacing, which is weak in the original state, the $(1\bar{1}\bar{2})$ re-reflection of 3.09 Å spacing disappear, and the $(11\bar{1})$ and the $(1\bar{1}\bar{1})$ reflections are not resolved from each other. In the process up to this stage, the values of the inter-planner spacings of all the reflections remain almost unchanged. In the 700°C heat-treated specimen, all reflections disappear, the original regular kaolin structure is entirely broken, and only a very diffuse and weak band is observable.

The structural transformation of Dry-branch kaolinite through heat-treatment follows practically the same process as that of Mesa Alta kaolinite. In the 545°C heat-treated specimen, its X-ray diagram indicates that the structure is in remarkably disorder in comparison with the 545°C heat-treated specimen of Mesa Alta kaolinite. The lattice water is lost, in this case, at a lower temperature than in the case of Mesa Alta kaolinite. This fact means that the velocity of the disintegration of the kaolinite structure attending the loss of the lattice water is related to the degree of crystallinity of the original mineral.

In Kibushi-clay, it is revealed in the light of X-ray traces that it has also the two elements of the progress and lowering of crystallinity as in the case of kaolinite. The progress of crystallinity of Kibushi-clay is remarkable up to 400°C heat-treatment. The lowering of crystallinity begins also at a low temperature as compared to that of kaolinite. In Kibushi-clay, its basal spacing slowly decreases with the rising of heat-treatment. This means that it is due to the loss of the inter-layer water which exists sporadically in this clay. In other words, it is because this clay originally contains the inter-layer water in its structure. This proves certainly that Kibushi-clay is low in crystallinity.

Differential Thermal Analysis.—Fig. 3 shows the differential thermal analysis curves in the process of heat-treatment of kaolinite. Table I shows the thermal data obtained from these curves.

In Mesa Alta kaolinite, as can be supposed, no endothermic reaction associated with the loss of the inter-layer water is observed. For the endothermic reaction (E_n) associated with the loss of the lattice water, the reduction in the area under the peak is not so remarkable between its original and 200°C heat-treated specimen; however, a slight reduction due to the loss of the lattice water becomes broad. In the 400°C heat-treated specimen, the area of this reaction reduces a little, and so does its height. In the 545°C heat-treated specimen, the area reduces con-

TABLE I

THERMAL DATA OF HEAT-TREATED SPECIMENS OF KAOLINITE

Sample	Treated temp.	E_n Temp. at peak	E_n Height of peak	E_x Temp. at peak	E_x Height of peak	E_x Breadth of peak
Kaolinite	original	604°C	16	966°C	39	5.1°C
(Mesa Alta,	200°C	598	14	964	41	4.8
N.M.)	400	593	11	964	44	4.2
	545	543	9	962	50	4.7
	700	—	—	962	63	5.0
Kaolinite	original	592	20	964	41	4.8
(Drybranch,	200	588	16	962	44	3.5
Geor.)	400	572	10	962	49	3.4
	545	559	3	963	58	3.9
	700	—	—	960	62	4.1

TABLE II

THERMAL DATA OF HEAT-TREATED SPECIMENS OF KIBUSHI-CLAY

Treated-temperatre	E_{n1} Temp. at peak	E_{n1} Height of peak	E_{n2} Temp. at peak	E_{n2} Height of peak	E_x Temp. at peak	E_x Height of peak	E_x Breadth of peak
original	130°C	1	574°C	14	945°C	13	10.5°C
200°C	120	1	572	12	943	14	10.3
400	120	1	570	12	944	13	10.5
545	—	—	561	5	944	14	10.4
700	—	—	—	—	942	18	9.6

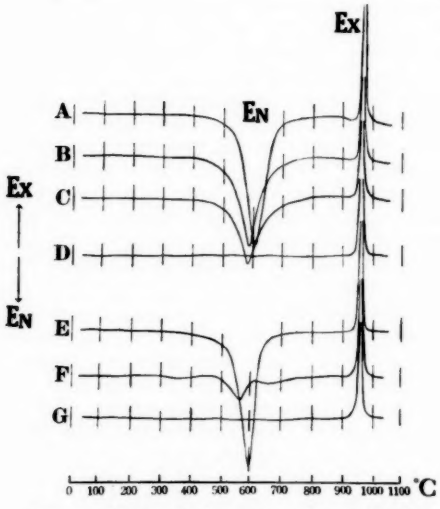

Fig. 3. Differential thermal analysis curves of heat-treated specimens of Mesa Alta and Drybranch kaolinite.
A, original Mesa Alta kaolinite
B, treated at 200°C
C, treated at 545°C
D, treated at 700°C
E, original Drybranch kaolinite
F, treated at 545°C
G, treated at 700°C

siderably. This means that the loss of the lattice water has considerably increased. In the 700°C heat-treated specimen, this endothermic reaction completely disappears.

Drybranch kaolinite behaves in a manner similar to Mesa Alta kaolinite. However, in the 545°C heat-treated specimen, the area of the endothermic reaction is small as compared with the 545°C heat-treated specimen of Mesa Alta kaolinite. This means that the crystallinity of its original sample is slightly lower than that of Mesa Alta kaolinite.

The final exothermic reaction (E_x) is due to the mullite nucleation. It is seen that the peak shifts slightly to the lower temperature side as the treated temperaturerises, and the peak height slowly increases. In the 700°C heat-treated specimen, the peak is considerably higher as compared with that of the original sample. From this fact, in spite of the fact that the X-ray diagram indicates that this state is amorphous, the rearrangement of ions is slowly occurring in the metakaolin matrix for the mullite nucleation. Generally, the breadth the exothermic reaction is defined as the breadth of temperature between the beginning point and the end

point. However, as these points are not so clear, in this study, the breadth at the point of the half value of the peak height is taken as the breadth of the peak. The breadth of the peak thus defined is considered to indicate the sharpness of the mullite nucleation. This breadth slightly reduces as the heat-treatment temperature rises. After reaching the minimum value, it increases again. Any definite conclusion can hardly be made from this phenomenon, however.

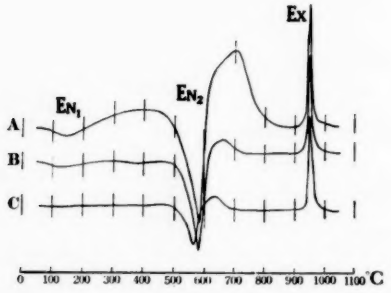

Fig. 4. Differential thermal analysis curves of heat-treated specimens of Kibushi-clay.

A, original clay
B, treated at 400°C
C, treated at 545°C

Fig. 4 shows the differential thermal analysis curves taken in the process of heat-treatment of Kibushi-clay and Table II gives data obtained from these curves. In the original sample, a weak endothermic reaction appears, associated with the loss of adsorbed or inter-layer water. In the 200°C and 400°C heat-treated specimens, the presence of weak but clear endothermic reaction is still observable. This might be due either to the fact that, after the heat-treatment it adsorbs water vapor so rapidly from the atmospheric air, or to the fact that the inter-layer water still remains even after the heat-treatment. The presence of such reactions in the heat-treated Kibushi-clay indicates that the degree of crystallinity of this clay is low. Similar phenomena are also observable in halloysite with a lower degree of crystallinity. For the endothermic and the exothermic reactions, the features in the variation of these reactions are similar to those of kaolinite, but these features are more pronounced.

Density.—The change in the density with the heat-treatment is shown in Fig. 5. The

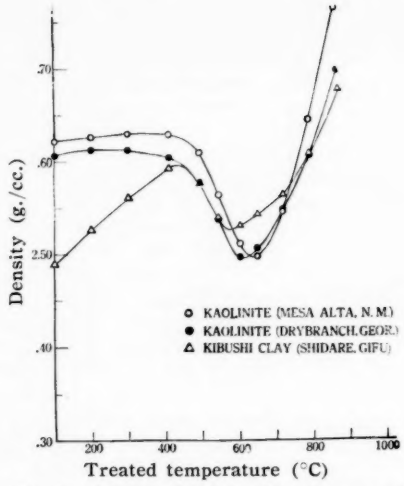

Fig. 5. Curves showing the changes of the density with the treated temperature.

density changes to a maximum through heat-treatment, then it falls and reaches the minimum value at the point where the lattice water is lost, finally it increases again rapidly. It can be seen that the higher the crystallinity is, the lower is the temperature correspoding to the maximum value on the density curve, and the higher is the temperature corresponding to the minimum value. This is correlated with the fact that as the internal degree of crystallinity is lower, the lattice water is lost at a lower temperature. The fact that the density of Kibushi-clay sharply increases in the early stage of heat-treatment is due to the presence of organic substance in it. The organic substance is slowly carbonized and oxidized through heat-treatment, and it is released as carbon dioxide. This corresponds to the fact that size of a broad exothermic reaction which appears just byond 600°C on the differential thermal analysis curve becomes smaller and smaller as the heat-treatment temperature rises.

The minimum value of density where the lattice water is lost, has no relation to the degree of crystallinity in either the kaolinite or the fireclay. Past the minimum point, the density increases almost in a straight line. The curve is steeper as the degree of crystallinity of the original sample is higher. It is evident that the rearrangement of ions is occurring in the lattice of the metakaolin state prior to

the mullite nucleation after the loss of lattice water. It is supposed that the stronger the structure of the original sample is, the faster and more perfect is the rearrangement of ions for the mullite nucleation.

Mechanism of Structural Change of Kaolinite and Kibushi-clay with Heat-Treatment.—The crystallinity of kaolin minerals consists of two elements as described in the previous paper[3], that is the degree of crystallinity in stacking of layers, and the internal degree of crystallinity in each layer. In the heat-treatment process of kaolinite and Kibushi-clay, there are two opposite processes. In the structural change of these clays in the early stage of heat-treatment, a minute water adsorbed on the surface of its crystallite or existing between micelles which is not detectable by th thermal curve, is lost gradually, and from this fact, it can be considered that its apparent crystallite size increases owing to the aggregation of several neighbouring crystallites. The apparent crystallite size becomes larger than that of the original crystallite. This tendency is remarkable particularly along the direction of *c*-axis which is perpendicular to the layer plane. Also the value of the density increases and the progress of the crystallinity is observable. In the next stage, the loss of the lattice water in the kaolin mineral takes place. At the beiginning of this reaction, the kaolin mineral transforms suddenly to metakaolin, and this lead to the amorphous structure in the X-ray diagram. In the metakaolin state which is realized prior to the mullite nucleation from the metakaolin, no observable indication for the structural change can be seen in the X-ray diagram. However, it is evident that, in the metakaolin structure, the rearrangement of ions takes place for the mullite nucleation. The rate of rearrangement depends on the crystallinity of the original sample. The higer the original crystallinity is, the more perfect is the rearrangement, and the more clearly can the mullite nucleation be seen. Compared with Kibushi-clay, in kaolinite the rearrangement proceeds more remarkably.

Summary

The structural change of kaolinite and Kibushi-clay with heat-treatment in the relatively low temperature region has been studied. It has been found that there are generally three processes, and that the structural change depends on the degree of crystallinity of the original samples.

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Electronic Structure of Phenol

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Effects of substituents on the electronic structures of reference hydrocarbons are very important from the standpoint of understanding their molecular properties. Hence, much work has been carried out in this domain. As far as the quantitative interpretation of the electronic spectra is concerned, satisfactory results have not yet been obtained, because of the difficulties in calculating the inter-electronic repulsion integrals.

In the previous papers[2], we studied the electronic structures of nitrogen heterocycles by semi-empirical *SCF* method with satisfactory results. In these cases, the repulsion integrals were approximated by the simplified formula.

In this paper, the semi-empirical calculation is applied to the electronic structure of phenol, assuming some further approximations.

Outline of the Method.—The method used is similar to that of Pariser-Parr[3]. It is based on the framework of the method for antisymmetrized products, in *LCAO* approximation, including configuration interaction, with only $2px$ electrons considered explicitly.

The molecular orbitals (*MO*), φ_i, are expressed in the form

$$\varphi_i = \sum_{\mu} c_{\mu i}\phi_{\mu} \tag{1}$$

where ϕ_{μ} is the μ th $2px$ atomic orbital (*AO*), and $c_{\mu i}$ are the coefficients to be determined by the variational method. We give each electron a molecular spin orbital (*MSO*) which is given by the product of coordinate function φ_i and spin function α or β. The configurational wave functions χ_n for the system are constructed from the antisymmetrized product, or Slater determinant, of these *MSO*'s. A given electronic state function, ψ_a, is represented by a linear combination of these configurational functions;

$$\psi_a = \sum_n A_{an}\chi_n \tag{2}$$

In the case of excited configuration, χ_n is written as ${}^1\chi_{i\to j}$ or ${}^3\chi_{i\to j}$ which denote a singlet or a triplet excited configuration caused by the excitation of an electron from an occupied orbital φ_i to a vacant orbital φ_j.

The energies of the electronic state are determined by solving a secular determinant

$$\mathrm{Det}\,|H_{mn}-\delta_{mn}E| = 0 \tag{3}$$

and the coefficients A_{an} are obtained by the solution of simultaneous equations

$$\sum_n A_{an}(H_{mn}-\delta_{mn}E) = 0 \tag{4}$$

where

$$H_{mn} = \int \chi_m^* \boldsymbol{H} \chi_n \mathrm{d}v$$

and $\delta_{mn}=1$ if m=n, $=0$ otherwise.

$\boldsymbol{H}$ is the complete electronic Hamiltonian operator determining the motion of the π-electrons, which is expressed in the form

$$\boldsymbol{H} = \sum_i H_{\mathrm{core}}(i) + \frac{1}{2}\sum_{ij}\frac{e^2}{r_{ij}} \tag{5}$$

According to the method described by Mulliken and Rieke[4], oscillator strength, f, associated with a transition between the ground state ψ_0 and an excited state ψ_i is calculated as

$$f = 1.085\times 10^{11} \times \omega_{0i} \sum_{T=x,y,z} (M^T{}_{0i})^2 \tag{6}$$

where ω_{0i} is the frequency of the transition in cm^{-1} and $M^T{}_{0i}$ is the transition moment defined by

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F. J. I. López-Vázquez, *An. Soc. Esp. Fis. y Qui.*, (Madrid), **51B**, 203 (1955) etc.

2) K. Nishimoto and N. Mataga, *Z. physik. Chem.* (N. F.) **12**, 335 (1957).
N. Mataga and K. Nishimoto, ibid., **13**, 140 (1957).

3) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953); ibid., **23**, 711 (1955).
R. Pariser, ibid., **24**, 250 (1956).

4) R. S. Mulliken and C. A. Rieke, *Rep. Progr. Phys.*, **8**, 231 (1941).

$$M_{0i} = \int \psi_0^* \sum_t e_t \mathbf{r}_t \psi_i \mathrm{d}v \qquad (7)$$

where e_t and $\mathbf{r}_t$ are the charge and the position vector of the t-th charged particle, respectively.

The π-electronic dipole moment, μ_π, is expressed in a similar form:

$$\mu_\pi = \int \psi_0^* \sum_t e_t \mathbf{r}_t \psi_0 \mathrm{d}v \qquad (8)$$

In our calculation, the following approximations are used.

1) As a set of *LCAO MO*'s, the conventional semi-empirical *MO*'s are chosen.

2) Differential overlap is neglected.

3) Values of some theoretical quantities are estimated by the empirical or semi-empirical procedure.

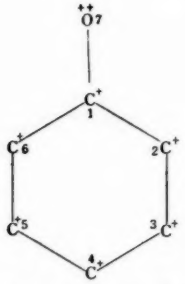

Fig. 1. Core structure of phenol.

4) The core structure of the molecule is shown in Fig. 1. Benzene ring is made up of the hexagone, with all nearest *C–C* distances equal to 1.390 Å. *C–O* distance is taken as 1.460 Å[5] which is the value of methyl acetate.

5) In the calculation of the configuration interaction, only the ground state configuration and the four lowest singly excited configurations are taken into account.

Calculation of Conventional Semi-empirical *MO*'s.—The core field of phenol pictured in Fig. 1 belongs to the symmetry group C_{2v}. It is, therefore, more convenient to express *MO*'s in terms of symmetry orbitals, σ_t, constructed from the *AO*'s according to the symmetry of the molecule;

$$\psi_i = \sum_t c_{ti} \sigma_t$$

σ_t's are written in the form,

$$\sigma_1 = \phi_1 \qquad \sigma_2 = \phi_2 + \phi_6 \qquad \sigma_3 = \phi_3 + \phi_5$$

$$\sigma_4 = \phi_4 \qquad \sigma_5 = \phi_7 \qquad (9)$$

$$\sigma_6 = \phi_2 - \phi_6 \qquad \sigma_7 = \phi_3 - \phi_5 \qquad (10)$$

The orbitals (9) belong to the representation B_1 and the orbitals (10) to A_2. The coefficients, c_{ti}, are determined by minimizing the expression for the energy, ε,

$$\varepsilon = \int \varphi^* H^e \varphi \mathrm{d}v \Big/ \int \varphi^* \varphi \mathrm{d}v$$

where H^e is the total effective Hamiltonian.

The matrix elements are assumed as follows,

i) When μ and ν are both carbon atoms,

$$H^e_{\mu\mu} = \int \phi_\mu^* H^e \phi_\mu \mathrm{d}v = \alpha$$

$$H^e_{\mu\nu} = \int \phi_\mu^* H^e \phi_\nu \mathrm{d}v = \beta \quad (\mu\nu: \text{neighbor})$$

$$H^e_{\mu\nu} = 0 \qquad (\mu\nu: \text{non-neighbor})$$

ii) When μ is an oxygen atom,

$$H^e_{77} = \alpha + \delta\beta$$

δ is determined to be 1.5 by the combination of the ionization potentials of CH_3OH and C_6H_6[6], setting the value of β equal to 3 eV[7].

iii) When μ is an oxygen atom and ν a carbon atom located at the position indicated by 1 in Fig. 1.

$$H^e_{71} = k\beta$$

where the value of k is chosen so as to bring the difference between the calculated energies of the highest occupied orbitals for benzene and phenol close to that between the observed ionization potentials[6] for them. Thus the suitable value is found to be 0.7.

The calculated orbital energies and the corresponding *MO*'s, using above mentioned parameters, are given in Table I.

The four *MO*'s, φ_1, φ_2, φ_3, and φ_4, are occupied by two electrons, respectively, and they form closed shells. The other three are vacant orbitals.

Semi-empirical Evaluation of Some Theoretical Quantities.—Molecular integrals appearing in eqs. 3 and 4 are expanded in terms of atomic integrals which are divided into two groups, one of the type of core integrals and one of the type of repulsion integrals. These quantities are adjusted by the empirical or semi-empirical procedure which is similar to that of Pariser-Parr, but somewhat different.

(1) By the assumption of zero differential overlap, only the two electron

5) J. M. O'Gorman, Jr., W. Shand and V. Schomaker, *J. Am. Chem. Soc.*, **72**, 4222 (1950).

6) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1997).

7) R. S. Mulliken, *Phys. Rev.*, **74**, 736 (1948).

TABLE I

CONVENTIONAL SEMI-EMPIRICAL *MO*'S OF PHENOL

Orbital energies in β	*MO*
2.1754	$\varphi_1=0.4955\sigma_1+0.3592\sigma_2+0.2860\sigma_3+0.2630\sigma_4+0.5134\sigma_5$
1.6266	$\varphi_2=0.1269\sigma_1-0.1423\sigma_2-0.3584\sigma_3-0.4407\sigma_4+0.7016\sigma_5$
1.0000	$\varphi_3=0.5000\sigma_6+0.5000\sigma_7$
0.7869	$\varphi_4=0.4692\sigma_1+0.3458\sigma_2-0.1971\sigma_3-0.5009\sigma_4-0.4606\sigma_5$
−1.0000	$\varphi_5=-0.5000\sigma_6+0.5000\sigma_7$
−1.0642	$\varphi_6=0.5733\sigma_1-0.2503\sigma_2-0.3070\sigma_3+0.5770\sigma_4-0.1566\sigma_5$
−2.0248	$\varphi_7=0.4353\sigma_1-0.4105\sigma_2+0.3958\sigma_3-0.3909\sigma_4-0.0864\sigma_5$

repulsion integrals of the type $(\mu\mu|\nu\nu)$ may be considered. These are assumed to be as follows,

$$(\mu\mu|\nu\nu)=\int\phi_\mu^*(1)\phi_\nu^*(2)e^2/\mathbf{r}_{12}\phi_\mu(1)\phi_\nu(2)\mathrm{d}v$$
$$=e^2/(a+r_{\mu\nu})$$

where $r_{\mu\nu}$ is the interatomic distance between μ and ν atoms. The parameter a is determined in the following way, using the valence state ionization potential, I_μ, and the electron affinity, A_μ, in the same valence state.

(a) For the case of homonuclear two centers, we put

$$e^2/a=(\mu\mu|\mu\mu)=I_\mu-A_\mu$$

(b) For the case of heteronuclear two centers, i. e., for carbon and oxygen, we take as e^2/a, simple arithmetic mean of e^2/a's for carbon and oxygen.

The values of I_μ and A_μ for carbon are found in the paper of Pritchard-Skinner[8]. For the case of oxygen, I_μ and A_μ may be equal to the second and the first ionization potentials, respectively, because as shown in Fig. 1 the oxygen core has doubly positive charges. Unfortunately, the second ionization potential of oxygen in the valence state has not yet been established. Assuming that the promotion energies from the second ionized state and the first ionized state of oxygen to their valence states are the same, $(I_\mu-A_\mu)$ obtained by the spectroscopic method may be equal to that of the valence state values. The spectroscopic values are found in Ref. (9). Using the above assumption, we find

$$a_{CC}=1.328\ \text{Å}$$
$$a_{CO}=0.889\ \text{Å}$$

For the carbon two centers, in order that our expression for $(\mu\mu|\nu\nu)$ may coincide with one computed by Slater's atomic orbital, the effective nuclear charge, Z, must be put equal to 2.036 at $r_{\mu\nu}=0$[10] and decrease with the increase of $r_{\mu\nu}$.

Since the σ-core is not a point charge, but consists of a nucleus and many electrons surrounding it, it stands to reason that Z approaches to unity with the increase of $r_{\mu\nu}$ considering that the screening of the electrons against the nucleus becomes more and more complete with the increase of $r_{\mu\nu}$. In many papers published hitherto, the effect of the variation of effective nuclear charge has been neglected. Treatment taking such an effect into consideration seems to be desirable.

(2) The core integrals, $H_{\mu\nu}^{\text{core}}$, are given by

$$H_{\mu\nu}^{\text{core}}=\int\phi_\mu^*(1)H_{\text{core}}\phi_\nu(1)\mathrm{d}v$$

Pariser-Parr have given the following expressions for $H_{\mu\nu}^{\text{core}}$

$$H_{\mu\mu}^{\text{core}}=-\sum_\nu(\mu\mu|\nu\nu)-A_\mu$$

$$H_{\mu\nu}^{\text{core}}=\beta_{\mu\nu}\qquad(\mu\nu:\ \text{neighbor})$$

$$H_{\mu\nu}^{\text{core}}=0\qquad(\mu\nu:\ \text{non-neighbor})$$

For the case of an oxygen atom, the value of A_μ is chosen somewhat arbitrarily in the following way. On the calculation of simple *MO*'s, we have taken the value of $\delta=1.5$ for H^e_{77}. $H^e_{\mu\nu}$'s formally correspond to the matrix elements of the Hartree-Fock Hamiltonian, $F_{\mu\nu}$, which are expressed by

$$F_{\mu\nu}=\int\phi_\mu^*\boldsymbol{F}\phi_\nu\mathrm{d}v$$

where $\boldsymbol{F}$ is the Hartree-Fock Hamiltonian which is composed of the core operator, $\boldsymbol{H}$, and an operator concerned with the electron interaction, $\boldsymbol{G}$. If we put $F_{77}=\langle Fcc\rangle+1.5\langle F_{12}\rangle$ and calculate, using the approximated formula proposed by

8) H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

9) C. E. Moore, "Atomic Energy Levels" Vol. 1 (1949), The National Bureau of Standards, Washington.

10) R. G. Parr and B. L. Crawford, *J. Chem. Phys.*, **16**, 1049 (1948).

Pople[11], A_μ amounts to 11.649 eV, where $<>$ means the simple arithmetic average about the relating matrix elements. In a similar way, if we put $H_{17}=0.7<F_{12}>$, it is found to be $\beta_{CO}=-2.115$ eV. The value of β_{CC} is the same as in the previous papers.

Results and Discussion

In the calculation of configuration interaction, the four lowest singly excited configurations, $\chi_{4\to5}$, $\chi_{4\to6}$, $\chi_{3\to5}$, and $\chi_{3\to6}$, and ground state χ_0 are taken into account. $\chi_{4\to5}$ and $\chi_{3\to6}$ belong to the irreducible representation B_2 and the other three to A_1. According to the symmetry consideration, the secular determinant of 5th degree is factorized into two determinants, one degree and one of 3rd degree. The computed energies of configurations and the interconfigurational matrix elements, using the above described semi-empirical quantities are given inTable II.

TABLE II
VALUES OF THE ENERGIES OF CONFIGURATIONS AND THE INTERCONFIGURATIONAL MATRIX ELEMENTS IN eV UNITS

$E(\chi_0)$	0	$(^1\chi_{3\to5}\|\boldsymbol{H}\|\chi_0)$	0.020
$E(^1\chi_{3\to5})$	6.556	$(^1\chi_{4\to6}\|\boldsymbol{H}\|\chi_0)$	0.049
$E(^1\chi_{3\to6})$	6.018	$(^1\chi_{3\to5}\|\boldsymbol{H}\|^1\chi_{4\to6})$	−0.313
$E(^1\chi_{4\to5})$	5.264	$(^1\chi_{4\to5}\|\boldsymbol{H}\|^1\chi_{3\to6})$	0.927
$E(^1\chi_{4\to6})$	5.770	$(^3\chi_{3\to5}\|\boldsymbol{H}\|^3\chi_{4\to6})$	−0.375
$E(^3\chi_{3\to5})$	3.610	$(^3\chi_{4\to5}\|\boldsymbol{H}\|^3\chi_{3\to6})$	−0.375
$E(^3\chi_{3\to6})$	4.638		
$E(^3\chi_{4\to5})$	3.914		
$E(^3\chi_{4\to6})$	3.280		

The calculated excitation energies and oscillator strengths are presented in Table III, in comparison with the observed values, and the corresponding electronic state wave functions are collected in Table IV.

TABLE III
CALCULATED AND OBSERVED EXCITATION ENERGIES (IN eV) AND OSCILLATOR STRENGTHS

	Excitation energies		Oscillator Strengths	
	Calcd.	Obsd.	Calcd.	Obsd.
$^1B_2^-$	4.640	4.59[a]	0.022	0.02[b]
$^1A_1$	5.662	5.89[a]	0.251	—
$^1B_2^+$	6.642	—	0.987	—
$^1A_1$	6.667	—	0.971	—
$^3A_1^+$	3.035	—	0	—
$^3B_2^+$	3.755	—	0	—
$^3A_1^-$	3.855	—	0	—
$^3B_2^-$	4.797	—	0	—

a) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).
b) R. S. Mulliken, Ref. 4).

As shown in Table III, the agreement between the calculated and the observed values is satisfactory and further im provement will be expected by including other excited configurations and adjusting the core parameters. It may be reasonable to interpret the spectra of phenol in the near-ultraviolet region as those of benzene perturbed by mobile lone pair electrons of the substituent. As shown in our calculation, this correspondence will be explained by considering only four excited configurations. It is interesting to note that in the case of benzene the state energies of $^3B_{2u}^-$ and $^1B_{2u}^-$ which is the radiation emitting state are the same, while in phenol the latter is higher than the former by 0.157 eV which is greater compared with kT. It may be regarded as the principal reason for the appearance of intense fluorescence of phenol, because the radiationless,

TABLE IV
ELECTRONIC STATE WAVE FUNCTIONS AND THEIR ENERGIES

Symmetry	State energy (in eV)	Wave function
A_1	−0.001	$^1\psi_0=\chi_0-0.0092\ ^1\chi_{4\to6}-0.0038\ ^1\chi_{3\to5}$
B_2	4.640	$^1\psi_1=0.8298\ ^1\chi_{4\to5}-0.5581\ ^1\chi_{3\to6}$
A_1	5.661	$^1\psi_2=0.0092\chi_0+0.9439\ ^1\chi_{4\to6}+0.3301\ ^1\chi_{3\to5}$
B_2	6.642	$^1\psi_3=0.5581\ ^1\chi_{4\to5}+0.8298\ ^1\chi_{3\to6}$
A_1	6.666	$^1\psi_4=0.0038\chi_0-0.3301\ ^1\chi_{4\to6}+0.9439\ ^1\chi_{3\to5}$
A_1	3.035	$^3\psi_1=0.8372\ ^3\chi_{4\to6}+0.5469\ ^3\chi_{3\to5}$
B_2	3.755	$^3\psi_2=0.9204\ ^3\chi_{4\to5}+0.3909\ ^3\chi_{3\to6}$
A_1	3.855	$^3\psi_3=0.5469\ ^3\chi_{4\to6}-0.8372\ ^3\chi_{3\to5}$
B_2	4.797	$^3\psi_4=0.3909\ ^3\chi_{4\to5}-0.9204\ ^3\chi_{3\to6}$

11) J. A. Pople, *Proc. Phys. Soc.*, **A68**, 81 (1955).

or thermal, transition is inhibited. The fact that the values of interconfigurational matrix elements among the ground configuration and the excited configurations are small gives us to understand that the calculated conventional semi-empirical *MO*'s are fairly close to the self-consistent field *MO*'s. The π-electronic dipole moment, invoking the assumption of neglect of differential overlap, is calculated as

$$\mu = 1.04\,\mathrm{D}$$

The π-electronic dipole moment should be obtained by subtracting vectorially the σ-electronic dipole moment from the total moment determined experimentally. Unfortunately, the σ-electronic dipole moment has not been estimated, because the information about the σ-electronic states, especially for the substituent, is not enough and, moreover, the σ-core is not rigid, but is affected by the π-electronic state. Hence, we will not discuss this further.

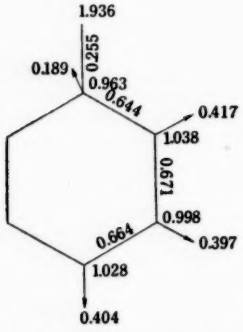

Fig. 2. Molecular diagram of phenol

The molecular diagram calculated by present treatment is shown in Fig. 2. From this diagram it may be expected that;

(i) In the electrophilic reactions, *o-p* substitution takes place.

(ii) The radical reactions take place preferentially at the *o*-positions.

(iii) The C—C bond distances are $C_1—C_2 > C_3—C_4 > C_2—C_3$.

(i) agrees with the experimental facts generally recognized. The information compared with (ii) or (iii) are not available. In the case of anisol which is similar to phenol in the π-electronic configuration, Suehiro[12] reported the order $o > p > m$ in the radical reactivities.

Summary

The electronic structure and spectra of phenol was studied from the semi-empirical point of view, using the *LCAO-ASP-CI-MO* method. The excitation energies and oscillator strengths of transitions to lower excited states were calculated. The agreement between the calculated and the observed values is very good. The charge distribution, bond orders and the π-electronic dipole moment are also calculated.

The authors express their appreciation to Mr. N. Mataga for many valuable discussions.

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12) T. Suehiro, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **72**, 301 (1951).

*Studies on the Thermal Decomposition of Cellulose Nitrate by Means of the Recording Thermal Balance**

By Takehiro ABE, Shōtaro TOBISAWA and Yōkan NOMURA

(Received July 10, 1958)

The products afforded by the thermal decomposition of cellulose nitrate have been investigated by many workers, recently by Wolfrom et al.[1-4] and by others[5,6]. The reaction of thermal decomposition has also been pursued by Will[7,8] and others[9,10] by means of measuring the gases evolved. However, no precise investigation by measuring the decomposition losses in weight has been made, because it is very difficult to measure the losses in weight successively with precision owing to the slow thermal decomposition.

In the present paper, therefore, we have, by means of a recording thermal balance with a high sensitivity, tried to follow the decomposition reaction of cellulose nitrate by raising the temperatures stepwise, after preheating at a low temperature below the decomposition point, or after keeping in reduced pressure.

Experimental

Cellulose nitrate was prepared by immersion of absorbent cotton (5 g.) into a mixed acid (303 cc.) of sulfuric acid (sp. gr.: 1.84, 171 cc.) and nitric acid (sp. gr.: 1.50, 110 cc.) at about 20°C for two hours. The product was washed thoroughly, and boiled with distilled water many times until a litmus paper did not show any trace of acidity on the wet cellulose nitrate. After being squeezed out, the cellulose nitrate was dried under vacuum for a day and kept in a desiccator. The cellulose nitrate contains 10.6% of nitrogen.

A recording magnetic balance devised by Hirone, Maeda and Tsuya[11] was used as our thermal balance without magnetic field. This balance, plotting automatically the loss in weight

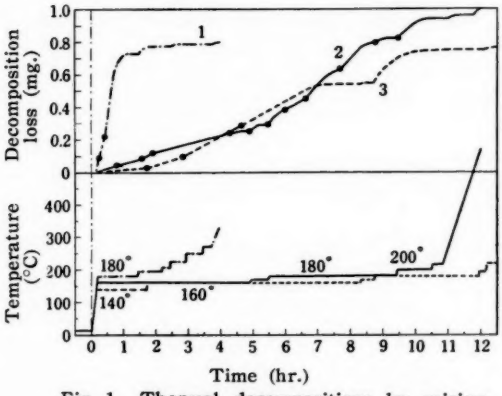

Fig. 1. Thermal decompositions by raising temperatures stepwise.

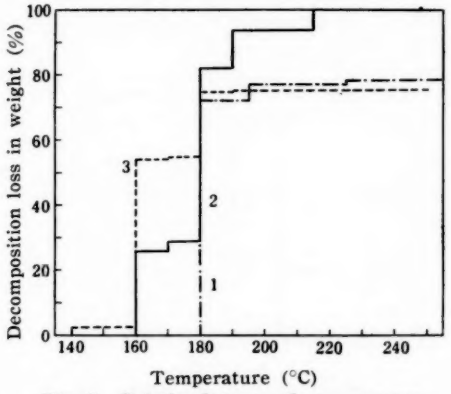

Fig. 2. Relation between the temperature and the decomposition loss in Fig. 1.

* Presented before the 10th Annual Meeting of the Chemical Society of Japan held at Tokyo in April, 1957.

1) M. L. Wolfrom et al., *J. Am. Chem. Soc.*, **77**, 6573 (1955).
2) M. L. Wolfrom et al., ibid., **78**, 4695 (1956).
3) M. L. Wolfrom, A. Chaney and P. McWain, ibid., **80**, 946 (1958).
4) F. Shafizadeh and M. L. Wolfrom, ibid., **80**, 1675 (1958).
5) R. W. Phillips, C. A. Orlick and R. Steinberger, *J. Phys. Chem.*, **59**, 1034 (1955).
6) G. Gelernter, L. C. Browing, S. R. Harris and G. M. Mason, ibid., **60**, 1260 (1956).
7) W. Will, *Fahresbericht der Centralstelle für wissenschaftlich-technische Untersuchungen*, **2** (1900).
8) W. Will, ibid., **3** (1900).
9) T. Hikita, *J. Ind. Explosives Soc., Japan*, **8**, 11 (1947).
10) E. K. Rideal and A. J. B. Robertson, "Third Symposium on Combustion and Flame", Reinhold, Baltimore (1949).
11) T. Hirone, S. Maeda and N. Tsuya, *Rev. Sci. Instr.*, **25**, 516 (1954).

vs. temperature curves of substances, was modulated to be able to indicate distinct differences of 0.02 mg. on a recorded chart. All samples in weight 1.0 mg. were packed in small quartz baskets and thermally decomposed under the pressure of about 50 mmHg, which was necessary for our present instrument.

Results and Discussion

Thermal decomposition by raising temperatures stepwise (Fig. 1).—The cellulose nitrate was decomposed at a constant temperature, and then at a higher temperature after a loss in weight stopped at the former temperature. Temperature was raised in this way. It is remarkable that several breaking points appear on each decomposition curve at constant temperatures. In Fig. 2 it is shown that a greater part of the cellulose nitrate decomposes at 160 and 180°C.

Thermal decomposition at constant temperature (Fig. 3).—As a matter of course, the higher the reaction temperature, the faster becomes the decomposition rate with an increase in the decomposition loss in weight. There appears no breaking point on the decomposition curve at 190°C.

The modes of decomposition at 140 and 150°C, giving only several per cent losses in weight, are different from those above 160°C. The loss in weight below 150°C is, therefore, is not considered to be due to the decomposition of cellulose nitrate itself, but is probably due to the volatilization of absorbed water, as mentioned below. Consequently, the decomposition temperature of the cellulose nitrate may be at about 160°C.

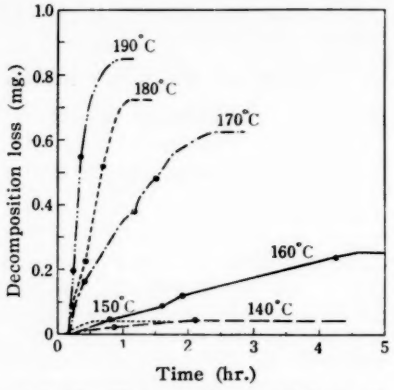

Fig. 3. Thermal decompositions at constant temperatures.

Thermal decomposition after preheating at low temperatures below the decomposition point.—a) In Fig. 4 it is shown that the thermal decomposition at 160°C after preheating at 140 or 150°C for an hour and a half gives a greater loss in weight than that without preheating.

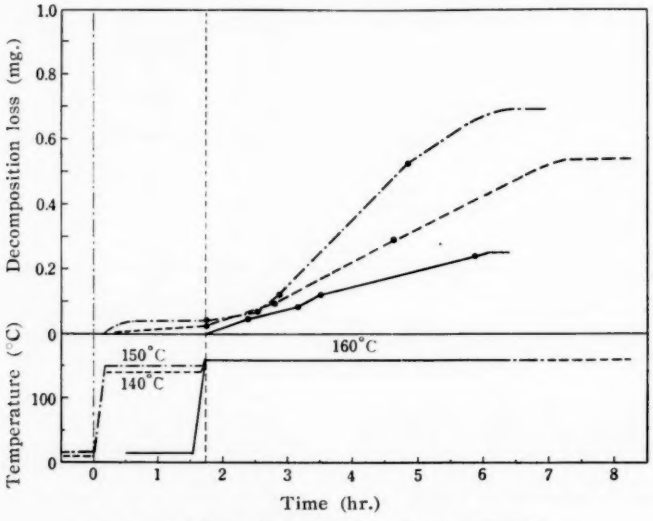

Fig. 4. Thermal decomposition after preheating.
——: not preheated.
------ and —·—: preheated at 140 and 150°C, respectively.

The sample preheated at 150°C decomposes more than that preheated at 140°C.

b) As shown in Fig. 5, the decomposition rate after preheating at 140°C for a long time is slower than that preheated at the same temperature for a short time. Both decompositions give about the same loss in weight.

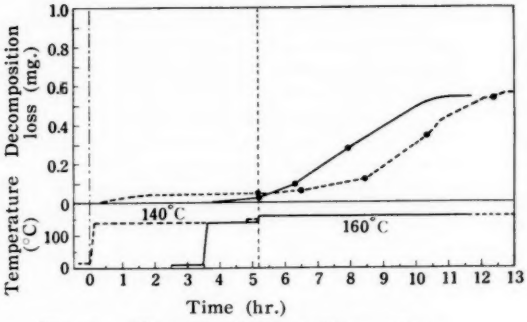

Fig. 5. Thermal decomposition after preheating at 140°C.
——: for a long time.
------: for a short time.

From the above results it is known that a thermal decomposition after preheating at a temperature slightly below the decomposition point for an hour or so results in greater decomposition loss in weight than that without preheating.

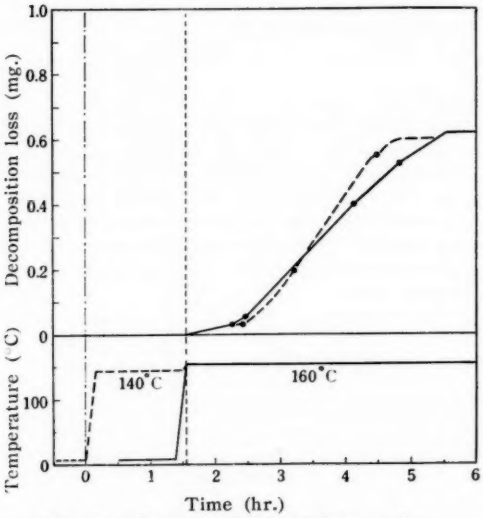

Fig. 6. Thermal decomposition after keeping under a reduced pressure and preheating.
——: not preheated.
------: preheated at 140°C.

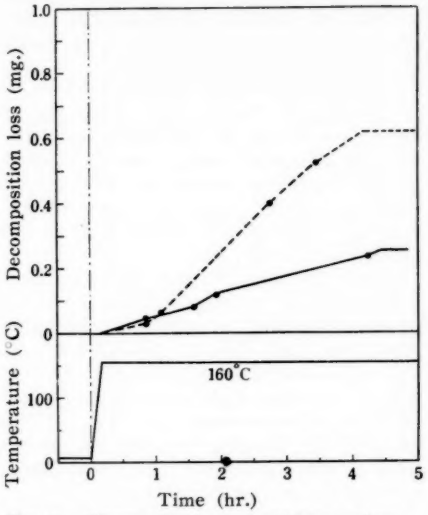

Fig. 7. Thermal decompositions after keeping under a reduced pressure.
——: without this procedure.
------: with this procedure.

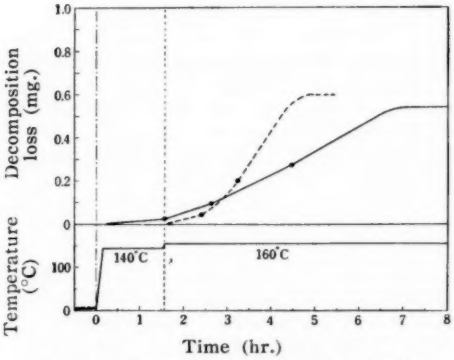

Fig. 8. Thermal decomposition after keeping under a reduced pressure and at 140°C.
——: only preheated.
------: low pressure and preheating.

Thermal decomposition after keeping a reduced pressure. — After being kept previously under reduced pressure of about 10^{-2} mmHg for four hours in the apparatus, the samples were decomposed under the same condition as measured before.

a) As seen in Fig. 6, the sample kept previously under a reduced pressure of 10^{-2} mmHg and preheated, decomposes rather faster than that kept only under a reduced pressure although both samples yield about the same loss in weight.

Heating the sample at 150°C results in no loss in weight, although the samples, which are not kept previously under a pressure of 10^{-2} mmHg, give several per cent loss in weight, as indicated in Figs. 1, 3, 4 and 5. These loss in weight below 150°C seems to be probably due to the volatilizations of water absorbed strongly by the cellulose nitrate in the air, since they can not be observed by keeping the samples previously under a pressure of 10^{-2} mmHg.

b) It is found from Fig. 7 that the sample kept previously in the reduced pressure yields a greater decomposition loss than that without any treatment.

c) As shown in Fig. 8, the decomposition of the sample kept previously under a reduced pressure and at 140°C, proceeds faster than that of the sample only preheated although there is no great difference between the decomposition losses of the two samples.

Summary

(1) The cellulose nitrate containing 10.6% of nitrogen decomposes above about 160°C. There appear distinct breaking points on the decomposition curves at constant temperatures slightly above the decomposition point. The higher the constant temperature of reaction, the greater becomes the decomposition loss in weight.

(2) The thermal decomposition after preheating at a temperature slightly below the decomposition point for an hour or so gives a greater loss of decomposition than that without preheating.

(3) The cellulose nitrate kept previously under a reduced pressure of about 10^{-2} mmHg yields a greater decomposition loss in weight than that without any treatment.

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Ring Cleavage in Liquid Sulfur Dioxide. I. Cleavage of Cyclic 1,2-Diketone Monoximes

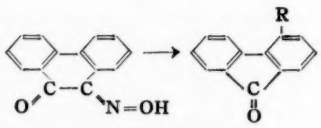
By Daisaburo MURAKAMI and Niichiro TOKURA

(Received July 7, 1958)

When a 1,2-diketone 1-monoxime is treated under the conditions of the Beckmann rearrangement, it is cleaved into two fragments, a cyano compound and a carboxylic acid[1,2]. This reaction, designated as the Beckmann rearrangement of the second order[2,3], is distinguished from the normal Beckmann rearrangement in its mechanism.

$$R-\overset{O}{\overset{\|}{C}}-\overset{NOH}{\overset{\|}{C}}-R' \longrightarrow RCOOH + R'CN$$

Usually the reaction is conducted in a basic solvent such as pyridine[2,4] at its refluxing temperature with an aromatic sulfonic acid or its chloride as the reagent[2]. Sulfuric acid, phosphoric acid, hydrochloric acid in acetic acid, and phosphorus compounds are used sometimes as the reagents but their use is limited because of inevitable side reactions. For example, 9,10-phenanthrenequinone 9-monoxime (II) gives a fluorenone derivative[1,3].



R=CN or $CONH_2$

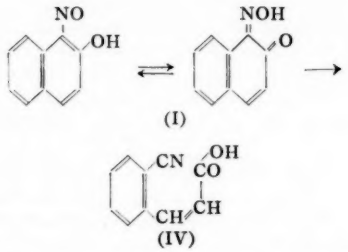
(II)

Considering the characteristic properties of liquid sulfur dioxide as solvent, the authors studied ring opening reactions of some cyclic 1,2-dione 1-monoximes in liquid sulfur dioxide, expecting smoother

1) a. E. Beckmann and A. Koster, *Ann.*, **274**, 15 (1893). b. E. Beckmann and O. Liesche, *Ber.*, **56**, 1 (1923). c. E. Beckmann and P. Wegerhoff, *Ann.*, **252**, 14 (1889).
2) A. Werner and A. Piguet, *Ber.*, **37**, 4293 (1904).
3) W. Borsche and W. Sander, ibid., **47**, 2825 (1914).
4) a. M. Gates, *J. Am. Chem. Soc.*, **72**, 228 (1950). b. B. Rapoport and J. Z. Pasky, ibid., **78**, 3788 (1956).

cleavages under milder conditions than in previously reported cases. Three typical diketone monoximes, viz., 1,2-naphthoquinone 1-oxime (I), 9,10-phenanthrenequinone 9-oxime (II) and tetralin-1,2-dione 2-oxime (III), were chosen.

Among various reagents tried, thionyl chloride only was found to effect the ring opening of I to *o*-cyanocinnamic acid (IV) in liquid sulfur dioxide. Toluenesulfonyl chloride and phosphorus pentoxide were slightly effective, but sulfur trioxide, sulfuric acid, phosphorus oxychloride, sulfuryl chloride, phosphorus pentachloride and aluminum chloride gave always resinous matters containing nitrogen.



Effects of the reaction time and temperature were studied with the results listed in Table 1.

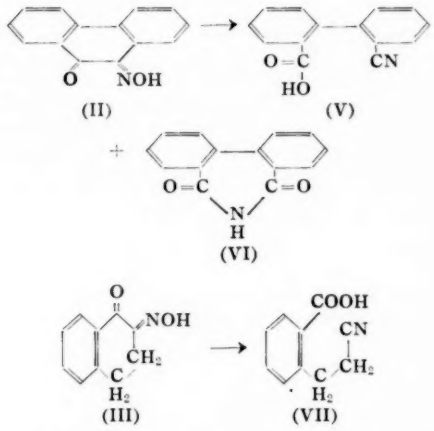
TABLE I

EFFECTS OF REACTION TIME AND TEMPERATURE ON RING OPENING OF 1,2-NAPHTHOQUINONE 1-OXIME IN LIQUID SULFUR DIOXIDE

Expt.	Thionyl chloride/naphthoquinone monoxime (Mole Ratio)	Reaction temp.°C	Reaction time	Yield (%)
1	3	−20	10 days	5
2	1	15	12 hrs.	10
3	1	15	10 days	40
4	1	50	6 hrs.	51
5	1	70	6 hrs.	54
6	2	70	6 hrs.	48
7	1	100	6 hrs.	46

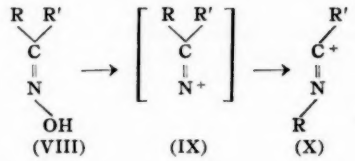
The best yield (54 percent) recorded in Table I is a great improvement if compared with the result obtained by Borsche[3] (1 g. of *o*-cyanocinnamic acid chloride from 17.3 g. of I). The temperature over 100°C caused a decrease in the yield of *o*-cyanocinnamic acid (IV) and an increase in resinous matters in the product.

9,10-Phenanthrenequinone 9-monoxime (II) was treated in the same way. By six hours' reaction at 70°C 2-cyanobiphenyl-2'-carboxylic acid (V) was obtained in a yield (60 percent) much greater than that reported previously[2]. As a by-product, diphenic acid imide (VI) was obtained in a yield of 11 percent. No fluorenone derivative was found in the reaction products[3].



No attempt has been reported on the cleavage of tetralin-1,2-dione 2-oxime (III). When the oxime was treated with thionyl chloride at 70°C for six hours in liquid sulfur dioxide, an almost quantitative yield (98%) of *o*-(2-cyanoethyl)benzoic acid (VII) was obtained. The experimental results are summarized in Table II.

The *trans*-migration in the Beckmann rearrangement has long been established[5]. The group in *anti* position to the hydroxyl group may shift to the nitrogen atom by rearrangement, which proceed, as is well recognized, through a nitrogen cation intermediate (IX) and intramolecular migration of the anion R.



In such a rearrangement it may not be possible for either a bulky group or a sterically strained group to take part. The carbon atom starred in XI could not migrate[6] owing to its double bond strain

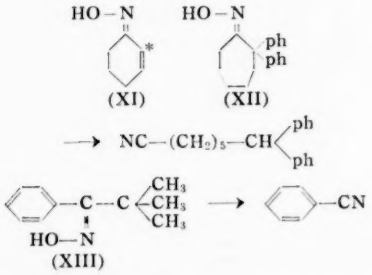
5) B. Jones, *Chem. Revs.*, **35**, 355 (1944).
6) F. J. Donat and A. L. Nelson, *J. Org. Chem.* **22**, 1107 (1957).

TABLE II

RING-OPENING OF 1,2-DIKETONEMONOXIMES WITH THIONYL CHLORIDE IN LIQUID SULFUR DIOXIDE

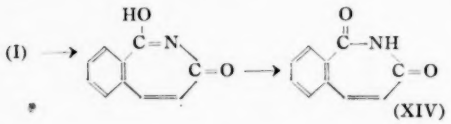
Compound	React. temp. (°C)	React. time (hr.)	Product	Yield (%)
1,2-naphthoquinone 1-oxime (I)	70	6	*o*-cyanocinnamic acid (IV)	54
9,10-phenanthrene-quinone 9-oxime (II)	70	6	2-cyanobiphenyl-2'-carboxylic acid (V) diphenic acid imide (VI)	60 11
tatralin-1,2-diketone 2-oxime (III)	70	6	*o*-(2-cyanoethyl)-benzoic acid (VII)	98

in a ring. Also ketoximes having bulky groups such as phenyl in XII[7] or *tert*-butyl[8] in XIII could not yield acid amides, and often gave cyano compounds.



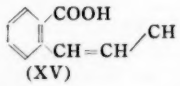
(XI) (XII) (XIII)

In naphthoquinone monoxime (I), the isonitrosomethylene group is sterically restricted in two ways, namely, by the condensation of a benzene ring and by the ring closure of groups on both its sides. Carbon atom 8a in I is inhibited from taking part in the rearrangement, and it may be impossible for carbon atom 2 to migrate to the nitrogen atom, since a steric interaction may prohibit the hydroxyl group from taking a *syn*-position to the condensed benzene ring, and thus the formation of dicarboxylic acid imide XIV may be improbable.



(XIV)

The present authors would not like to consider the dicarboxylic acid imide (XIV) as a precursor or an intermediate to *o*-cyanocinnamic acid (IV), because then one more final product (XV) would be expected from the imide (XIV).



(XV)

In the present study each cleavage gave only one kind of cyano acid, which resulted from a cleavage between the carbonyl group and the isonitrosomethylene group and a migration of the hydroxyl group. No isonitrile was found in the reaction product.

The only explanation for such a cleavage was presented by Blatt and Barnes[9] in 1934. However, little can be said regarding the mechanism of the cleavage reaction of the cyclic dione monoxime system, except some explanation of the cause which hinders the normal Beckmann rearrangement from taking place.

A superior method for preparing cyanocarboxylic acids by the cleavage in liquid sulfur dioxide may find a wide application in synthetic organic chemistry. Experiments in such a direction are now in progress.

Experimental

Solvent, reagents and apparatus.—Commercial liquid sulfur dioxide was distilled after dehydration with concentrated sulfuric acid[10]. Commercial reagents of pure grade were used. The reaction was carried out in a glass pressure bottle as reported in the preceding papers[11].

1,2-Naphtoquinone 1-oxime (I).—The oxime was synthesized by nitrosation of β-naphthol according to the method of C. S. Marvel and P. K. Porter[12], and recrystallized from ligroin. Brown crystals, m.p. 108°C. Yield 82%.

Ring cleavage of I to *o*-cyanocinnamic acid (IV).—Into a mixture of 5 g. of oxime I (0.03 mole) and 100 ml. of liquid sulfur dioxide, 5 g. of thionyl chloride (0.03 mole) in 30 ml. of

7) R. E. Lyle and J. L. Fielding, ibid., **20**, 623 (1955).
8) R. F. Brawn and N. M. Van Gulick, *J. Am. Chem. Soc.*, **77**, 1094 (1955).
9) A. H. Blatt and R. P. Barnes, ibid., **56**, 1148 (1934).
10) D. Murakami and N. Tokura, This Bulletin, **31**, 431 (1958).
11) N. Tokura, R. Asami and R. Tada, *Sci. Rep. of Res. Inst., Tohoku Univ.*, **A8**, 149 (1956).
12) C. S. Marvel and P. K. Porter "Organic Syntheses", Coll. Vol. I, p. 403 (1941).

liquid sulfur dioxide was introduced. The mixture was heated on a water bath at 70°C for 6 hours, when it became dark green in color. After the reaction was completed, sulfur dioxide was removed by evaporation. The residue was dissolved in 150 ml. of chloroform, and the acidic substance was extracted with 250 ml. of 1 N sodium bicarbonate solution. The extract was acidified to pH 3 with concentrated hydrochloric acid. *o*-Cyanocinnamic acid (IV), which separated out, was recrystallized from methanol. White plates, m. p. 254~255°C (reported as 254°C by Werner[2]). Yield, 2.7 g. (54%).

Anal. Found: C, 69.36; H, 4.24; N, 8.38. Calcd. for $C_{10}H_7O_2N$: C, 69.36; H, 4.07; N, 8.09%.

The results obtained under various conditions are listed in Table I.

To a mixture of 30 ml. of ethanol and 10 ml. of concentrated sulfuric acid was added 0.5 g. of IV and the solution was refluxed for several hours. Ethyl *o*-cyanocinnamate was obtained from the reaction mixture by treating it as usual. White plates (from ethanol), m. p. 57~57.5°C. Yield, 0.3g.

Anal. Found: N, 7.05. Calcd. for $C_{12}H_{11}O_2N$: N, 6.96%.

9,10-Phenanthrenequinone 9-oxime (II).—The quinone was synthesized by oxidizing phenanthrene with chromic acid[13]. The quinone was then monoximated with hydroxylamine hydrochloride by modifying Pschorr's[14] procedure. Five grams of monoxime II was obtained from 10 g. of the quinone.

Ring cleavage of II to 2-cyanobiphenyl-2'-carboxylic acid (V).—In 100 ml. of liquid sulfur dioxide 3 g. (0.015 mole) of the oxime (II) was dissolved and the solution was treated with 1.8 g. (0.015 mole) of thionyl chloride in 30 ml. of liquid sulfur dioxide at 70°C for 6 hours. After evaporating off the solvent, the residue was dissolved in alcohol. The alcoholic solution was filtered and the filtrate was treated with 1 N sodium bicarbonate solution. By acidifying the solution 2-cyanobiphenyl-2'-carboxylic acid (V) was precipitated, and recrystallized from benzene. White pillars, m. p. 169~171°C, (reported[2] m. p. 171~172°C). Yield, 1.8 g. (60%).

Anal. Found: C, 75.06; H, 4.23; N, 6.05. Calcd. for $C_{14}H_9O_2N$: C, 75.32; H, 4.06; N, 6.28%.

In 10 ml. of methanol 0.3 g. of V was dissolved and hydrogen chloride was introduced into the mixture. By cooling, methyl 2-cyano-biphenyi-2'-carboxylate was precipitated. Recrystallized from 50% ethanol, white pillars, m.p. 79~80°C. (reported[2] m.p., 79~80°C). Yield, 0.2 g.

From the part insoluble in cold ethanol, a white crystalline subtance, m.p., 217~218°C, was obtained by sublimation in a yield of 0.5 g. (11%) and proved to be diphenic acid imide (VI) by the mixed melting point with an authentic specimen[15].

Anal. Found: N, 6.04. Calcd. for $C_{14}H_9O_2N$: N, 6.28%.

When the reaction was conducted at 15°C, the yields of V and VI decreased to 33% and 5%, respectively.

Tetralin-1,2-dione 2-oxime (III).—Tetralone was prepared from tetralin by air oxidation[16] and the ketone was then treated with isoamyl nitrite to give tetralin-1, 2-dione 2-oxime (III) according to the method of Straus and Eckhard[17] with a slight modification. Pale yellow crystals, m.p. 140~142°C. Yield, 45%.

Cleavage of III to *o*-(2-cyanoethyl) benzoic acid (VII).—A mixture of 3 g. (0.017 mole) of III and 2 g. (0.017 mole) of thionyl chloride in 130 ml. of liquid sulfur dioxide was treated for 6 hours at 70°C as stated above. After evaporating off the solvent, the residue was washed with dilute sodium bicarbonate solution and the solution was acidified. Recrystallization of the precipitates from water afforded 2.9 g. (98%) of *o*-(2-cyanoethyl) benzoic acid (VII). White plates, m. p. 111~112°C.

Anal. Found: C, 68.71, H, 5.04, N, 8.15. Calcd. for $C_{10}H_9O_2N$: C, 68.56, H, 5.18, N, 8.00%.

As a proof of the structure of VII, VII was decarboxylated to β-phenylpropionitrile (XVI), which was then hydrolyzed to β-phenylpropionic acid (XVII) in the following way.

Decarboxylation of VII to β-phenylpropionitrile (XVI).—A mixture of 2 g. (0.012 mole) of VII, 1 g. of copper powder and 30 g. of quinoline was refluxed with stirring for four hours. Evolution of carbon dioxide was observed. The mixture was filtered and the filtrate was diluted with 200 ml. of chloroform. The solution was washed with 5 percent hydrochloric acid and with 2 percent aqueous sodium hydroxide solution successively, and dried with anhydrous sodium sulfate. After the evaporation of the solvent (chloroform), the residue was subjected to a distillation in vacuo and β-phenylpropionitrile (XVI) was obtained as a pale yellow liquid of b.p. 115~117°C (7 mm.) (reported[18] b.p., 114~118°C (8 mm.)). Yield, 1.1 g, (73%).

Anal. Found; C, 77.75, H, 6.27, N, 9.19. Calcd. for C_9H_9N; C, 82.40, H, 6.92, N, 10.68%.

XVI was not pure enough for analysis. It was hydrolyzed to β-phenylpropionic acid (XVII).

Hydrolysis of XVI to β-phenylpropionic acid (XVII).—A mixture of 0.5 g. of XVI in 5 ml. of 10 percent alcoholic potash was refluxed for ten hours. Then the reaction mixture was poured onto ice water and extracted with chloroform. The solution was dried and evaporated. The residue was recrystallized from water to obtain 0.3 g. (53%) of XVII as white needles, m. p. and mixed m.p. with an authentic specimen, 48~49°C. (reported[19] m. p. 47.5~48.0°C).

Anal. Found: C, 70.42, H, 6.68. Calcd for $C_9H_{10}O_2$: C, 71.98, H, 6.71%.

13) R. Wendland and J. LaLonde, *Org. Synth.*, **34**, 76 (1954).
14) R. Pschorr, *Ber.* **35**, 2734 (1902).
15) N. Tokura and S. Anazawa, *Sci. Rep. of Res. Inst. Tohoku Univ.*, **A9**, 239 (1957).
16) R. B. Thompson, "Organic Syntheses" Coll. Vol. II, 995 (1943).
17) F. Straus and W. Eckhard, *Ann.*, **444**, 162 (1925).
18) V. Grignard, E. Bellet and Ch. Courtot, *Annales de chimie et de physique*, [9], **4**, 43 (1915).
19) A. W. Ingersoll, "Organic Syntheses", Coll. Vol, I, p. 311 (1941).

Summary

1,2-Diktone monoximes were subjected to treatment with thionyl chloride in liquid sulfur dioxide to obtain cyanocarboxylic acids in good yields.

The authors wish to express their thanks to Befu Chemical Industries Co. Ltd., for the donation of liquid sulfur dioxide, and to Miss Yoko Endo for the microanalyses. The present investigation was supported by a grant from the Ministry of Education.

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Studies on Meso-ionic Compounds. VIII[1]*. Oxidation of Sydnones*

By Mutsuko HASHIMOTO and Masaki OHTA

(Received June 3, 1958)

Substitution reactions of 3-phenylsydnone and the behavior of 3-phenyl-4-bromosydnone suggest us that the sydnone nucleus is aromatic in character to a considerable extent. As many instances are known where a methyl substituent in aromatic heterocycles is oxidized to a carboxylic group, it seemed possible to oxidize 4-methylsydnones to corresponding 4-carboxylic acid derivatives. Although this was not realized, we found an interesting rearrangement during the oxidation of several sydnones.

The oxidation of 3-phenyl-4-methlsydnone (Ia) with potassium permanganate in acetone did not afford the expected carboxylic acid, but the oxidative cleavage of sydnone ring occurred, affording acetophenone. The same reaction product was also obtained by oxidation of Ia with potassium permanganate in aqueous pyridine or with aqueous hydrogen peroxide in acetic acid. In each case a slight evolution of gas was observed. The results obtained here suggest that the rearrangement of a phenyl group in 3-position of 3-phenyl-4-methylsydnone from nitrogen (3-position) to carbon (4-position) occurred in the course of the oxidation process.

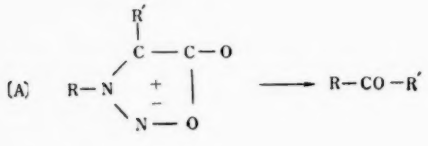

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Fig. 1.

a; $R=C_6H_5$, $R'=CH_3$
b; $R=C_6H_5$, $R'=H$
c; $R=p\text{-}CH_3\cdot C_6H_4$, $R'=H$
d; $R=R'=C_6H_5$
e; $R=o\text{-}CH_3\cdot C_6H_4$, $R'=H$

A reaction of the same type also occurred when 3-phenylsydnone (Ib) and 3-*p*-tolylsydnone (Ic) were treated with aqueous hydrogen peroxide in acetic acid at room temperature, affording benzaldehyde and *p*-tolualdehyde, respectively.

When the same procedure was applied to 3,4-diphenylsydnone (Id) and 3-*o*-tolylsydnone (Ie), however, the expected ketone or aldehyde was not obtained, but the starting materials were recovered unchanged. When 3,4-diphenylsydnone was heated with a mixture of hydrogen peroxide and acetic acid, a very small amount of phenol was obtained, which was identified by Liebermann's nitroso test, coloration on addition of ferric chloride and formation of tribromophenol.

The oxidation of 3-phenylsydnone (IIa) with potassium permanganate in acetone gave, quite unexpectedly, 3,4-diphenylsydnone (IIIa) and benzaldehyde. The 3,4-diphenylsydnone obtained here was identical with a specimen prepared by the method reported by Baker et al.[2]. The oxidation of 3-*p*-tolylsydnone (IIb)

1) Part VII of this series, H. Kato and M. Ohta, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zassi*), **78**, 1653 (1957).

2) W. Baker, W. D. Ollis and V. D. Poole, *J. Chem. Soc.*, **1949**, 307.

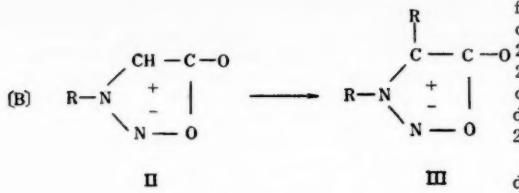

Fig. 2.

a: $R=C_6H_5$(=Ib) a: $R=C_6H_5$(=Id)
b: $R=p\text{-}CH_3\cdot C_6H_4$(=Ic) b: $R=p\text{-}CH_3\cdot C_6H_4$

with potassium permanganate also gave 3,4-di-*p*-tolylsydnone (IIIb).

The results obtained above are not quite sufficient for a deduction concerning the reaction mechanism. However, from a consideration of the result obtained in the case of 3-phenyl-4-methylsydnone, it might be assumed that only 3-arylsydnone which has no substituent in 4-position could give 3, 4-diarylsydnone by the action of potassium permanganate, and that 4-substituted sydnone was oxidized to ketone. On the basis of this fact, it seems reasonable to conclude that the intermolecular rearrangement described above was preceded by the formation of aryl radical by the action of potassium permanganate on sydnone, followed by the attack of the aryl radical on 4-position of the unchanged sydnone. The value of the free valence in 4-position of sydnone lends some support to this consideration; namely, according to Orgel et al.[3], a value of 0.562 is calculated, which corresponds with that of free valence in 9- or 10-position of anthracene where radical substitution occurs readily. For the determination of the mechanism of such reactions, however, a more detailed investigation will probably be required.

Two novel types of the rearrangement reaction presented in this paper, have not yet been observed with heterocyclic compounds.

Experimental

Oxidation of 3-Phenyl-4-methylsydnone (Ia) with Potassium Permanganate.—a) To a solution of 4.4 g. of Ia, prepared by Earl's method[4], in 200 cc. of acetone was added portionwise 7.9 g. of finely powdered potassium permanganate with stirring at room temperature. After being kept overnight, the precipitated manganese dioxide was filtered off and the filtrate was evaporated. From the residue was obtained an oily product boiling at 68°/17 mm., 2,4-dinitrophenylhydrazone of which melted at 239~240°, and did not show any melting point depression on admixture with the authentic 2, 4-dinitrophenylhydrazone of acetophenone (m. p. 238°).

b) In aqueous pyridine, 4.4 g. of Ia was oxidized with 7.9 g. of potassium permanganate at room temperature. After being kept overnight, the precipitated manganese dioxide was filtered off and the filtrate was evaporated under reduced pressure. The residue was extracted with ethanol and the ethanol was removed. The crude reddish brown oil, dissolved in benzene and passed through an alumina column, gave 0.34 g. of Ia and an oily product, 2,4-dinitrophenylhydrazone of which did not show any melting point depression on admixture with the authentic 2,4-dinitrophenylhydrazone of acetophenone.

Oxidation of Ia with Hydrogen Peroxide.—To a solution of 8.8 g. of Ia in 20 cc. of glacial acetic acid was added 8.4 g. of aqueous 30% hydrogen peroxide and this was kept standing at room temperature for 29 hours. The reaction mixture was diluted with 80 cc. of water, neutralized by sodium carbonate and extracted with ether. The extracts were washed with aqueous sodium bicarbonate and dried. An oily product (1.3 g.) gave phenylhydrazone (m. p. 101°) and 2, 4-dinitrophenylhydrazone (m. p. 239°) which did not show any melting point depression on admixture with those of acetophenone, respectively.

Oxidation of 3-Phenylsydnone (Ib) with Hydrogen Peroxide.—a) To a solution of 4 g. of Ib, prepared by our method[5], in 25 cc. of glacial acetic acid was added 4.2 g. of aqueous 30% hydrogen peroxide. After standing at room temperture for 24 hours, the reaction mixture was treated by the same procedure as described above. An oily product obtained gave phenylhydrazone (m. p. 155~156°) and 2, 4-dinitrophenylhydrazone (m. p. 233°), both of which showed no melting point depression on admixture with the authentic samples obtained from benzaldehyde.

b) When Ib was treated by the same procedure as described in a) except that the reaction time was 5 hours, 70% of Ib was recovered.

Oxidation of 3-*p*-Tolylsydnone (Ic) with Hydrogen Peroxide.—When a mixture of Ic, prepared by Baker's method[2], and 20 cc. of glacial acetic acid and 2.1 g. of aqueous 30% hydrogen peroxide was kept standing at room temperature for 24 hours, and then treated by essentially the same method as described above, *p*-tolualdehyde was obtained and identified as phenylhydrazone (m. p. 112°) and 2, 4-dinitrophenylhydrazone (m. p. 230°).

3-*o*-Tolylsydone (Ie).—A suspension of 29 g. of *o*-tolylglycine, prepared by Steppes' method[6], in 350 cc. of water was treated with 20 cc. of concentrated hydrochloric acid and cooled at 0°. A solution of 13 g. of sodium nitrite in 35 cc. of

3) L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951).
4) J. C. Earl and A. W. Mackney, *J. Chem. Soc.*, **1935**, 899.
5) M. Hashimoto and M. Ohta, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zassi*), **78**, 181 (1957).
6) F. Steppes, *J. prakt. Chem.*, [2] **62**, 491 (1900).

water was added dropwise with vigorous stirring. After an hour dark brown viscous oil had separated. The oil was dissolved in ether, washed with water and dried and the ether was evaporated. Reddish brown oil was obtained, giving a positive Liebermann's nitroso test. Yield 37.2 g. In 200 cc. of acetic anhydride was dissolved 37.2 g. of the crude nitroso acid, kept standing for three days at room temperature, and water was then added. The solid which separated out was collected and washed with aqueous sodium carbonate and water. White flakes were obtained, m. p. 86°, yield 6.8 g.. An analytical sample was prepared by recrystallization from water, m. p. 96° (the reported melting point[7] is 89°). *Anal.* Found: N, 15.66. Calcd. for $C_9H_8O_2N_2$: N, 15.90%.

Reaction of 3-*o*-Tolylsydnone (Ie) with Hydrogen Peroxide.—A mixture of 1.1 g. of Ie and 20 cc. of glacial acetic acid and 1.05 g. of aqueous 30% hydrogen peroxide was kept standing at room temperature for 24 hours, and then diluted with water. White crystals separated out (m. p. 96°, 0.57 g.), undepressed on admixture with Ie.

When the filtrate was neutralized with sodium carbonate, and extracted with ether and the ether was evaporated, 0.16 g. of Ie was still recovered.

Reaction of 3,4-Diphenylsydnone (Id) with Hydrogen Peroxide.—When a mixture of 24 g. of Id and 20 cc. of glacial acetic acid and 1.7 g. of aqueous 30% hydrogen peroxide was treated with the same procedure as described above, 2.22 g. of Id was recovered.

b) A mixture of 2.4 g. of Id and 20 cc. of glacial acetic acid and 1.7 g. of aqueous 30% hydrogen peroxide was heated for 5 hours at 90°, and diluted with 100 cc. of water. The crystals which separated out were recrystallized from ethanol, m. p. 181~181.5°, undepressed by admixture with Id. Yield 0.61 g..

The acidic filtrate was neutralized with sodium bicarbonate, and extracted with ether and then the ether was evaporated. A very small amount of oil with a smell of phenol was obtained, giving a positive Liebermann's nitroso test and a red ferric chloride reaction, and afforded a bromo-derivative which showed no melting point depression on admixture with the authentic sample of tribromophenol.

Oxidation of 3-Phenylsydnone (IIa) with Potassium Permanganate.—To a solution of 8.1 g. of IIa in 400 cc. of acetone was added portionwise 15.8 g. of finely powdered potassium permanganate with stirring at room temperature. After being kept overnight, the precipitated manganese dioxide was filtered off and the acetone was removed. From the residue light yellow crystals separated out, and were collected and recrystallized from ethanol. Pale yellow prisms, m. p. 183~184.5°, were obtained and did not show any melting point depression on admixture with 3,4-diphenylsydnone (IIIa), prepared by Baker's method[8]. Yield 1.1 g., 22%.

The filtrate (2.1 g.) gave 2,4-dinitrophenylhydrazone, m. p. 233°, undepressed on admixture with the authentic 2,4-dinitrophenylhydrazone of benzaldehyde.

Oxidation of 3-*p*-Tolylsydnone (IIb) with Potassium Permangante.—To a solution of 5.28 g. of IIb in 240 cc. of acetone was added 9.48 g. of finely powdered potassium permanganate. The reaction mixture was treated by essentially the same method as described above, and the yellow crystals obtained were recrystallized from ethanol. Light yellow flakes, m. p. 156.5~157° (the reported melting point[8] for 3,4-di-*p*-tolylsydnone (IIIb) is 156~157.5°). Yield 0.82 g., 20.6%.

Anal. Found: N 11.01. Calcd. for $C_{16}H_{14}O_2N_2$: N, 10.52%.

The authors are grateful to Mr. Asaji Kondo for carrying out the microanalyses.

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7) J. Hadáček et al., *Publs. fac. sci. univ. Masaryk Cišlo*, **357**, 257 (1954).

8) W. Baker, W. D. Ollis and V. D. Poole, *J. Chem. Soc.*, **1950**, 1542.

Electron Diffraction Investigation on Tropone[1]

By Katsumi KIMURA, Satoshi SUZUKI, Masao KIMURA and Masaji KUBO

(Received June 19, 1958)

In recent years, considerable interest has been directed to the determination of the molecular structures of compounds having a seven-membered carbon ring by electron diffraction[2,3] as well as by X-ray crystal analysis[4-6]. However, the investigations that have hitherto been made have dealt with tropolone and its derivatives. Tropone is the simplest compound having a cycloheptatriene ring and for this reason it is most suitable for the determination of the geometric form of this carbon ring. According to the results of dipole moment measurements, this compound is characterized by special resonance stability[7], which is expected to be revealed more directly by the measurements of bond lengths. Recent advances in the experimental technique of electron diffraction by gas molecules have made it possible to obtain the values of structural parameters with high precision. In view of this situation, the present investigation was undertaken in order to determine the structure of tropone by measuring the scattered intensity using the sector-microphotometer method. In this study, it was also possible to determine the magnitudes of vibrational amplitudes of some atom pairs.

Experimental

The electron diffraction photographs of the molecule were taken using a rotating sector. The present studies were made with an r^2-sector provided with a beam trap. The trap was 20 mm. long and 2 mm. in radius[8]. The use of this trap was effective in eliminating extraneous scatterings. The apparatus used was essentially the same as that previously employed[9]. The camera distance was 12 cm. long. The electron beam passing through slits was focused onto a photographic plate, the focused spot being about 0.1 mm. in diameter. The electron wavelength was determined by calibration with a gold foil to be equal to about 0.063 Å.

The sample was kindly furnished by Professor Nozoe of Tohoku University[10]. At room temperature, tropone is a liquid having a low vapor pressure. In order to obtain vapor pressures required for taking good diffraction photographs, it was necessary to use a high-temperature nozzle. Therefore, a number of capillary tubes containing the sample were placed in the furnace. The furnace and the nozzle were maintained at about 100°C during exposures of photographic plates to diffraction beams. The vapor was led through the nozzle and was projected across the electron beam. The pressure of the sample was controlled by regulating the temperature of the reservoir.

In order to apply Karle's method[11] of density-intensity calibration, several sets of two sector photographs were taken, different exposures (about 2 : 1) being employed in each set under otherwise the same conditions. Microphotometric tracings were made on the diffraction patterns using a recording microphotometer. The conversion of the observed densities into intensity curves made after Karle's method[11].

Analysis of Data

Radial Distribution Curve. — In the first place, the structure of the molecule was studied by the radial distribution method, although the correlation method was employed later. The radial distribution curve, $f(r)$ was calculated from the experimental molecular intensity curve according to the equation[12],

1) A part of the results presented here has been reported at a meeting of the Chemical Society of Japan held in Sendai in October 1956. A preliminary report has been published in a short communication: K. Kimura, S. Suzuki, M. Kimura and M. Kubo, *J. Chem. Phys.*, **27**, 320 (1957).

2) E. Heilbronner and K. Hedberg, *J. Am. Chem. Soc.*, **73**, 1386 (1951).

3) M. Kimura and M. Kubo, This Bulletin, **26**, 250 (1953). M. Kubo, M. Kimura and K. Kimura, ibid., **27**, 455 (1954).

4) J. M. Robertson, *J. Chem. Soc.*, **1951**, 1222.

5) Y. Sasada, K. Osaki and I. Nitta, *Acta Cryst.*, **7**, 113 (1954).

6) Y. Sasada and I. Nitta, ibid., **9**, 205 (1956).

7) Y. Kurita, T. Nozoe and M. Kubo, This Bulletin, **24**, 10 (1951). Y. Kurita, S. Seto, T. Nozoe and M. Kubo, ibid., **26**, 272 (1953).

8) S. Shibata, The Eighth Symposium on X-ray and Electron Diffraction, Osaka, November 1956.

9) M. Kimura, K. Kimura and S. Shibata, *J. Chem. Phys.*, **24**, 622 (1956).

10) T. Nozoe, S. Seto, Y. Kitahara, M, Kunori and Y. Nakayama, *Proc. Japan Acad.*, **26**, 38 (1950).

11) I. L. Karle and J. Karle *J. Chem. Phys.*, **17**, 1052 (1949). J. Karle and I. L. Karle, ibid., **18**, 957 (1950).

12) See, for example, P. A. Schaffer, Jr., V. Schomaker and L. Pauling, *J. Chem. Phys.* **14**, 659 (1946).

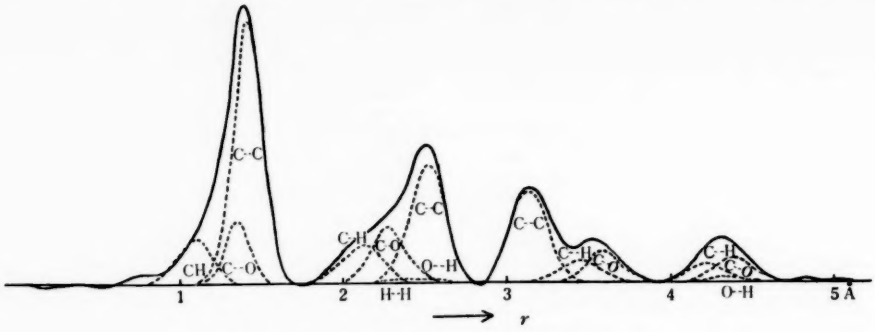

Fig. 1. Radial distribution curve for tropone.

$$f(r) = \sum_{s=0}^{s_{max}} sM(s)\exp(-bs^2)\sin(sr)$$

where $M(s)$ is the molecular scattering intensity and other symbols have their usual significances. The experimental $M(s)$ curve was obtained by dividing the total intensity by the background intensity, corrections being made for the interference arising from non-nuclear scattering[13]. Fig. 1 shows the radial distribution curve computed with an artificial damping factor chosen so as $\exp(-bs_{max}^2) = 0.1$.

The values of distance were evaluated by fitting Gaussian peaks to the experimental curve. The first peak at about 1.4 Å is due mainly to seven bonded C-C distances (C_1-C_2, C_2-C_3, etc.) and has some contributions from bonded C=O and C—H distances (C_2—H_2, etc.) appearing on the left-hand side of the prominent peak. Here, the carbon atoms composing the ring and the hydrogen atoms attached to it are numbered as shown in Fig. 2. If

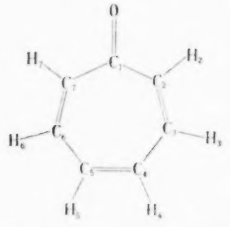

Fig. 2. The numbering of carbon and hydrogen atoms in a tropone molecule.

it is assumed that all the bonded C—C distances are equally long and that C—H distances are also the same, the C-C peak can be located at 1.405 Å and the most probable values for the C—H and C=O distances are 1.09 and 1.26 Å, respectively. The mean amplitude of vibration has been found to be 0.050 Å for the C—C distances. Even if there is some spread in the values of C—C distances, the mean amplitude for each C—C bond will be essentially the same as the above-mentioned value derived on the assumption that all the C-C distances are equally long. However, it is not possible from this analysis to decide whether or not there are small differences among the bonded C-C distances. For example, even if the individual C-C distances were shifted by less than about ±0.01 Å, to give an average distance 1.405 Å, no appreciable change would result in either the position of the C-C peak or in the mean amplitude.

The second peak at about 2.5 Å can be assigned mainly to the short C···C (C_1-C_3, C_2-C_4, etc.), short C···O (C_2-O and C_7-O) and short C···H (C_1-H_2, etc.) distances. Contributions from short O···H and short H···H distances are negligibly small. The second peak was decomposed into three Gaussian peaks in the following way. The analysis of the first peak showed that even if the carbon ring is distorted from a regular heptagon form, the distortion is slight. Therefore, the short C···O and C···H distances were first assumed to be 2.26 and 2.12 Å, respectively, on the basis of the result from the first peak. Then, the corresponding peaks were subtracted from the total curve, the mean amplitudes of 0.070 and 0.100 Å being used for the C···O and C···H peaks, respectively. The subtraction yielded a peak corresponding to the short C···C distance capable of being fitted with a Gaussian peak centered at 2.52 Å. Next, the reverse procedure was followed, the C···C peak

13) L. S. Bartell and L. O. Brockway, ibid., **23**, 1854 (1955).

thus obtained was subtracted from the total curve and then the remaining portion was separated into two peaks, one at 2.28 Å for the C···O distance and the other at 2.10 Å for the C···H distance. The separation was made so that each of these peaks has an area proportional to the number of distances times $z_i z_j / r_{ij}$. Thus the mean amplitude turned out to be 0.066 and 0.110 Å for the C···O and C···H distances, respectively. If the seven-membered carbon ring is assumed to be undistorted from a regular heptagon form, the short nonbonded C···C, C···O and C···H distances are calculated on the basis of the observed C—C and C—H distances to be equal to 2.53, 2.26 and 2.12 Å, respectively, in good agreement with the experimental values.

The third peak at about 3.15 Å is due almost solely to long nonbonded C···C (C_1-C_4, etc.) distances and a weak neighboring peak at about 3.5 Å to long C···O (C_3-O and C_6-O) and long C···H (C_1-H_3, etc.) distances. This composite peak was decomposed in the same manner as for the second peak mentioned above. In this case, the separation of the C···C peak was scarcely affected by the peak corresponding to the long C···O distances. The observed values for these three distances, 3.15, 3.58 and 3.46 Å, are in fair agreement with the respective values, 3.16, 3.60 and 3.45 Å, calculated from the model of a regular heptagon form. The mean amplitudes of the C···C distance is 0.079 Å. The remaining peak at 4.3 Å corresponds for the most part to longer nonbonded C···C (C_4-O and C_5-O) and C···H (C_1-C_4, etc.) distances. The distances for the Gaussian peaks resulting from the proper decomposition of the composite peak are 4.40 and 4.20 Å, while the values calculated on the assumption of the undistorted carbon ring are 4.39 and 4.23 Å, respectively.

TABLE I. COMPARISON OF THE OBSERVED DISTANCES WITH THOSE CALCULATED ON THE BASIS OF A REGULAR HEPTAGON MODEL.*

Bond type	Atom pair	Distance (Å) obs.	Distance (Å) calc.
Bonded distances	C—H	1.09	
	C=O	1.26	
	C—C	1.405	
Short nonbonded distances	$C_1 \cdots H_2$	2.10	2.12
	$C_2 \cdots O$	2.28	2.26
	$H_2 \cdots H_3$	(2.35)	2.35
	$O \cdots H_2$	(2.43)	2.43
	$C_1 \cdots C_3$	2.52	2.53
Long nonbonded distances	$C_1 \cdots C_4$	3.15	3.16
	$C_1 \cdots H_3$	3.46	3.45
	$C_3 \cdots O$	3.58	3.60
Longer nonbonded distances	$C_1 \cdots H_4$	4.20	4.23
	$O \cdots H_3$	(4.37)	4.37
	$C_4 \cdots O$	4.40	4.39

* Assumed values are enclosed in parentheses.

Table I shows a comparison of the observed distances from the radial distribution curve with the calculated distances for the molecule having an undistorted regular heptagon ring. It is apparent that the observed and calculated values are in good agreement with each other. In addition, a test for the relative areas of peaks in the radial distribution curve shows an agreement within 5% between the observed and calculated values. Thus, from the analysis of the experimental curve, it was found that the curve could be interpreted adequately on the basis of a coplanar model having a regular heptagon carbon ring. It is important to note that, if the molecule is not planar, some peaks in the radial distribution curve would have appeared in shorter distances than those actually observed. Accordingly, it seems to be adequate to conclude that this molecule is definitely coplanar.

Choice of the Molecular Models.— Before the construction of theoretical curves of molecular intensity is attempted, it is necessary to define the molecular parameters required for the complete description of selected models. The parameters were chosen for the present purpose on the basis of the results obtained from the radial distribution curve. A tropone molecule is presumed to have a plane of symmetry perpendicular to the molecular plane. Consequently, the structure has C_{2v} symmetry and the geometric configuration of heavy atoms can be completely described by giving seven independent parameters, because the carbon ring of the molecule involves four nonequivalent C—C distances. The following seven parameters were chosen in order to determine the structure having the C_{2v} symmetry: C=O, C_1-C_2 (=C_1-C_7), C_2-C_3 (=C_7-C_6), C_3-C_4 (=C_6-C_5) and C_4-C_5 distances along with the x- and y-components of the $C_1 \cdots C_3$ (=$C_1 \cdots C_6$) distance, which determine the positions of C_3 and C_6 atoms relative to C_1 atom. The C_1-C_2 and C_3-C_4 distances will be almost equal to or longer than the C_2-C_3 and C_4-C_5 distances, since it is likely that the latter bonds have a more or less pronounced

double bond character compared with the former. Therefore, two extreme cases were taken up for the C-C distances: First, all the C-C distances are equally long and secondly, C_1-C_2=C_3-C_4=1.43 Å., C_2-C_3=1.38 Å and C_4-C_5=1.37 Å. These distances give an average value that is almost the same as the observed value. As regards the position of the C_3 atom, six points were chosen on a circle of 0.04 Å in radius with its center at the position of the C_3 atom for the regular heptagon ring. The values for the C=O distance were selected at 1.21, 1.26 and 1.31 Å. Since the mean amplitude is an important factor in determining the maxima and minima of intensity curves, various values of mean amplitudes were used for C-C atom pairs as shown in Table II.

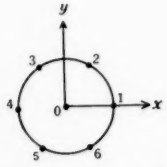

Fig. 3. Various positions of the C_3 atom for "distorted" models. The origin of rectangular coordinates coincides with the position of the C_3 atom in the regular heptagon ring.

TABLE II. VARIOUS SETS OF THE MEAN AMPLITUDES OF C-C ATOM PAIRS IN 10^{-3} Å.

Set	1	2	3	4	5	6	7	8
C—C	50	50	50	50	50	50	50	50
Short C···C	55	55	55	65	65	75	75	85
Long C···C	60	80	100	80	100	80	100	100

Comparison of Theoretical and Experimental Intensity Curves.—In calculating theoretical intensity curves, various atom pairs could be grouped into four different types: (1) C—C, short C···C and long C···C, (2) C=O, short C···O, long C···O and longer C···O, (3) C—H, short C···H, long C···H and longer C···H, and (4) nonbonded O···H and H···H. The distances belonging to types 1 and 2 determine the framework of the molecule. The contributions from the distances of type 1 dominate the greater portion of the intensity curve, i. e., 60~80% of the total intensity depending upon the s values. They practically determine the positions of maxima and minima of the intensity curve. On the other hand, the distances of type 2 affect the form of a number of shelves in the intensity curves in such a remarkable manner that the C=O distance can be evaluated with fair accuracy. The intensity curves are relatively insensitive to changes in the bond lengths and the valency angles involving hydrogen atoms, i. e., to changes in distances belonging to

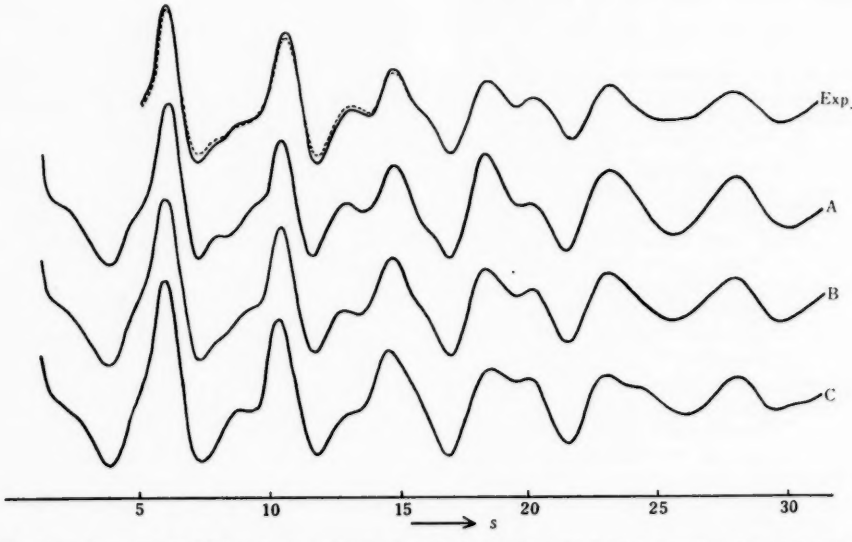

Fig. 4. Comparison between experimental and theoretical intensity curves for tropone. In the experimental curve, the full line represents the intensity curve that was corrected for the constant coefficient[13] and the broken line represents the uncorrected curve.

type 3. The changes of ±0.02 Å in the bonded C—H distances have no appreciable effect on the intensity curves. Therefore, the C—H distance, 1.09 Å, derived from the radial distribution curve was used throughout. The effect of the separations of type 4 is inappreciable. In calculating theoretical intensity curves, all terms of the function[12,13],

$$sM(s)=\sum_{ij}(Z_iZ_j/r_{ij})\exp(-b_{ij}s^2)\sin(sr_{ij})$$

were included. Theoretical curves were calculated using various values for the selected parameters mentioned in the foregoing section and were compared with the observed curve. From this comparison, it became clear that the observed curve could be adequately interpreted in terms of the heptagon model and the C=O distance of 1.26 Å determined from the radial distribution curve was also very satisfactory. An increase or decrease in this distance by 0.05 Å resulted in considerable changes in the intensity curve. Fig. 4 illustrates the experimental curve together with the theoretical curves A, B and C computed for the regular heptagon ring with C=O=1.21, 1.26 and 1.31 Å, respectively. As to the mean amplitudes of the C-C distances, set 4 in Table II was found to give the best values consistent with the experimental curve. As can be seen from Fig. 4, curves A and C show departures from the observed one: for instance, a shelf at about $s=13$ and a maximum at $s=20$ are too high in curve A and too low in curve C. The portion of the experimental curve between $s=7.5$ and 9.4 shows small humps. Curve B well reproduces this feature, whereas curves A and C do not. The value of s/s_{exp} averaged over ten maxima and minima in curve B is 1.000 with an average deviation of 0.0040.

A number of curves for various "distorted" models were also carefully compared with the experimental curve. It was shown that none of the curves for the "distorted" models reproduced the experimental curve better than the heptagon model in regard to the following points. The major points were: First the shape of shelves in the region, $s=7.0\sim9.5$ and at about 14 and 15.5, secondly the shape of the minimum at about $s=19$ and lastly the intensity relations in the region, $s=7\sim24$.

Results and Discussion

The structural results obtained for a tropone molecule are summarized in Table III. Attention should be called to the fact that the experimental radial distribution curve and various features in the experimental intensity curve can be precisely interpreted in terms of a regular heptagon model. Unlike a tropolone molecule, a tropone molecule having only one oxygen atom resonates among a single electronic structure without a formal charge on any atoms of the molecule and various electronic structures of dipolar character. Accordingly, it is likely that the C-C distances are not equally long, but have a more or less pronounced single or double bond character. Therefore, as mentioned above, various "distorted" models were tried. It was found that, provided that the average C-C distance was equal to 1.405 Å, disparities of the order of 0.04 Å in C-C bond lengths as well as of about 10° in ∠CCC valency angles did not lead to models giving theoretical intensity curves very different from that of the "undistorted" model. However, it is of particular interest that the best agreement was obtained between the observed intensity curve and the final theoretical intensity curve for the simple "undistorted" regular heptagon model.

TABLE III. STRUCTURE OF A TROPONE MOLECULE.

Essentially regular heptagon carbon ring
C···C = 1.405±0.005 Å with $\langle l^2\rangle^{1/2}=0.050\pm0.005$ Å
C=C = 1.26±0.02 Å with $\langle l^2\rangle^{1/2}=0.038$ Å
C—H = 1.09±0.03 Å

It is also of interest to observe that the values determined for the C—C and C···H distances in tropone are very close to those reported for benzene[14,15]. The mean C-C distance of 1.405 Å in tropone is almost identical with that in tropolone determined as 1.40 Å[2] and 1.39 Å[3] by the electron diffraction method and with those in various crystalline modifications of tropolone derivatives studied by X-ray analysis, i.e., 1.40 Å[4] in copper(II) tropolonate (=cupric tropolone), 1.40 Å[5] in tropolone hydrochloride and 1.414 Å[6] in sodium tropolonate.

Layton, Kross and Fassel[16] showed that the stretching frequency of carbon-oxygen bonds in carbonyl compounds plotted against the bond length can be represented by a smooth curve. With the aid of this

14) I. L. Karle, ibid., **20**, 65 (1952).
15) A. Almennigen and O. Bastiansen, Research Correspondence, 9 (September 1956).
16) E. M. Layton, R. D. Kross and V. A. Fassel, ibid., **25**, 135 (1956).

relationship, it is possible to estimate the C=O bond length in a tropone molecule by interpolation from the observed vibrational frequency[17] of the C=O bond. The interpolation indicates that the C=O bond distance is about 1.27 Å, in excellent agreement with the value observed in the present work. Further, an approximate method[18] enables one to evaluate the mean amplitude from the vibrational frequency as $\langle l_{CO}^2 \rangle^{1/2} = 0.039$ Å, which is also in good agreement with the observed value. In Table IV, the mean amplitudes of C-C atom pairs in tropone are compared with those in benzene.

TABLE IV. COMPARISON OF THE MEAN AMPLITUDES IN Å FOR C-C ATOM PAIRS BETWEEN TROPONE AND BENZENE MOLECULES.*

Atom pair	Tropone	Benzene	
		Karle[19]	Bastiansen[19]
C—C	0.050(1.405)	0.055(1.393)	0.0454
Short C···C	0.066(2.52)	0.067(2.41)	0.054
Long C···C	0.079(3.15)	0.075(2.786)	0.061

* The corresponding equilibrium distances in Å are enclosed in parentheses.

17) E. Kloster-Jensen, N. Tarköy, A. Eschenmoser and E. Heilbronner, *Helv. Chim. Acta*, **39**, 786 (1956).
18) K. Kimura and M. Kimura, *J. Chem. Phys.*, **25**, 352 (1956).
19) O. Bastiansen and S. J. Cyvin, *Nature*, **180**, 980 (1957).

Summary

The electron diffraction photographs of tropone in the gaseous state were taken with an s^2-sector. The data of the scattered intensity was analyzed by means of the radial distribution method as well as by the correlation method. The investigation of the molecule has led to the conclusion that the molecule assumes an essentially co- planar structure having a regular heptagon ring. The most probable values for the bond distances are: C—C=1.405±0.005 Å, C=O=1.26±0.02 Å and C···H=1.09±0.03 Å.

We wish to express our thanks to Professor T. Nozoe for providing us with the sample used in the present investigation, to Professor R. Uyeda for his permission to use a microphotometer and to Mr. H. Morimoto for his help in carrying out microphotometric tracings. We are also to the Ministry of Education for financial assistance.

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*Über die Kupfer- und Nickelkomplexsalze des Salicylaldehyd-benzoylhydrazons und seiner Oxyderivate**

Von Hiroshi OHTA

(Eingegangen am 12. Juli, 1958)

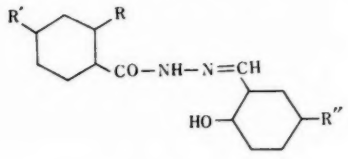
Seit der Entdeckung der tuberkulostatischen Wirkung von Isonikotinsäurehydrazid, sind verschiedene Säurehydrazide synthetisiert worden. Vor kurzem haben Buu-Hoï und seine Mitarbeiter[1] mitgeteilt, dass die Oxybenzoesäurehydrazide und ihre *N*-Salicyliden-Derivate in vitro ziemlich stark tuberkulostatisch sind, was darauf zurückzuführen sei, dass sie mit Schwermetallen, die für Enzyme nötig sind, Komplexsalze bilden können. Die Komplexsalze dieser Verbindungen sind aber bisher noch nicht beschrieben worden.

In der vorliegenden Mitteilung sollen die Kupfer- und Nickelkomplexsalze einiger Salicylaldehyd-aroylhydrazone berichtet werden. Als Ausgangsstoffe für die Darstellung wurden Salicylaldehyd-benzoylhydrazon, -2-methoxybenzoylhydrazon, -4-oxybenzoylhydrazon, -2-oxybenzoylhydrazon, -2-oxy-4-aminobenzoylhydrazon und

* Organische Metallkomplexsalze. II. Vorgetragen auf der XI. Versammlung der Japanischen Chemischen Gesellschaft in Tokyo, am 4. April, 1958. I. Mitteilung: H. Ohta, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zassi*), **78**, 1608 (1957).
1) Ng. Ph. Buu-Hoï und Mitarbb., *J. Chem. Soc.*, **1953**, 1358.

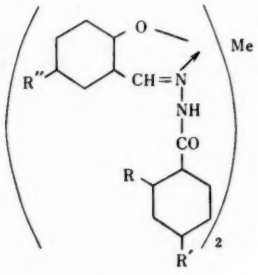
5-Bromsalicylaldehyd-2-oxybenzoylhydrazon herangezogen, von denen Salicylaldehyd-2-oxy-4-amino-benzoylhydrazon und 5-Bromsalicylaldehyd-2-oxybenzoylhydrazon bisher unbekannt waren.

Reagieren die Salicylaldehyd-aroylhydrazone in der Keto-Form I mit dem Kupfer- oder Nickel-Ion, so sollten sie, wie Salicylaldehyd-phenylhydrazon, Komplexsalze von der Formel II bilden.



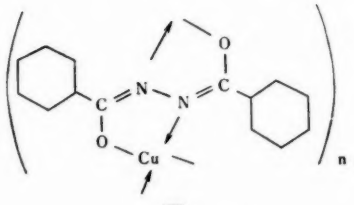
I

(1) R=R'=R''=H.
(2) R=OCH_3, R'=R''=H.
(3) R=R''=H, R'=OH.
(4) R=OH, R'=R''=H.
(5) R=OH, R'=NH_2, R''=H.
(6) R=OH, R'=H_2, R''=Br.

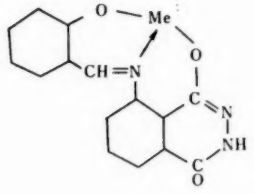


II

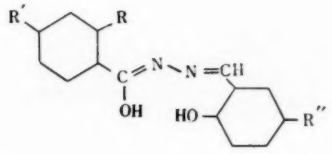
Me=Cu oder Ni



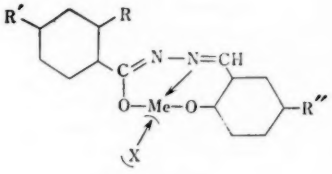
III



IV



V



VI

X=NH_3 oder C_5H_5N

Da aber Benrath[2] schon früher ein Kupferkomplexsalz des Dibenzoylhydrazins von der Formel III erhielt, und Tsumaki und seine Mitarbeiter[3] neuerdings Kupfer- und Nickelkomplexsalze des 5-Salicylidenamino-1, 4-dioxo-tetrahydrophthalazins IV darstellten, so ist es zu erwarten, dass die Salicylaldehyd-aroylhydrazone auch in der Enol-Form V reagieren können.

Gehen sie nun in die Enol-Form über, dann können die Atome bzw. Atomgruppen so aufgestellt werden, dass die Bildung der Komplexsalze von der Formel VI sterisch nicht verhindert wird;

$$-C(OH)=N-N=CH-\overset{|}{C}=(OH)C-$$

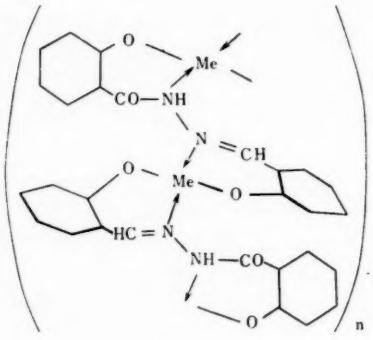
kann auf einer Ebene liegen und die interatomischen Abstände sind zur Ausbildung von Wasserstoffbrücke begünstigt (Abb. 1). Die der VI analogen Komplexsalze sind schon von mehreren Autoren beschrieben worden, so z. B. die Kupferkomplexsalze des 2-Salicylidenaminophenols[4], 2,2'-Dioxy-azobenzols[4], Salicylaldehyd-thiosemicarbazons[6] und des Salicyliden-salicylamins[6], sowie die Nickelkomplexsalze des 2-Salicylidenaminophenols[4] und des Salicylaldehyd-thiosemicarbazons[5].

2) N. Benrath, *J. prakt. Chem.*, [2] **107**, 223 (1924).
3) T. Tsumaki und Mitarbb., *Reports of the Faculty of Science, Kyushu University, Chem. Sec.*, **1**, 161 (1950).
4) P. Pfeiffer und Mitarbb., *J. parkt. Chem.*, [2] **149**, 217 (1937).
5) V. Hovorka und Mitarbb., *Collection Czechoslov. Chem. Communs.*, **15**, 267 (1950).
6) M. Yamaguchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **74**, 261 (1953).

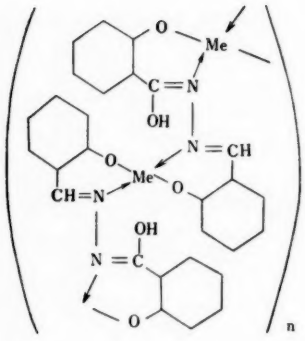
Abb. 1. Kalottenmodell des Salicylaldehydbenzoylhydrazons (Enol-Form).

Die Komplexsalze wurden nach der Beschreibung im Versuchsteile durch Gemischen der Hydrazone und der Metallacetate in Ammoniakwasser oder Ammoniakwasser-Alkohol-Gemische dargestellt. Die Kupfersalze bilden bräunlichgrüne Kristalle, die Nickelsalze orangerote Kristalle. Nach den analytischen Daten kommt ihnen eine allgemeine Formel $C_{14}H_7N_2O_2RR'R''Me \cdot NH_3$ zu (In bezug auf R, R' und R'', siehe Formel I). Das Kupferkomplexsalz von Salicylaldehyd-2-methoxybenzoylhydrazon enthält jedoch kein Ammoniak. Wenn die Komplexsalze in Vakuum erhitzt werden, dann geben die Kupfersalze Ammoniak völlig ab; die Farbe schlägt nach Olivgrün um. Die Nickelsalze dagegen erleiden keinen Gewichtsverlust. Von Interesse sind die Kupferkomplexsalze von Salicylaldehyd-2-oxybenzoylhydrazon und -4-oxybenzoylhydrazon, sowie das Nickelkomplexsalz von Salicylaldehyd-2-oxy-4-aminobenzoylhydrazon; jedes enthält ausser dem Ammoniak auch 1 Mol. Wasser, und, beim Erhitzen in Vakuum geben die Kupfersalze anfangs Wasser dann Ammoniak ab. Das Nickelsalz verliert aber nur das Wasser und verwandelt sich zu orangerotem Pulver. Daher muss das Wasser mit den Molekülen lockerer gebunden sein als das Ammoniak. Die Farbe des wasserfreien Kupfersalzes von Salicylaldehyd-2-oxybenzoylhydrazon ist der des wasserhaltigen ähnlich; diejenige des wasserfreien Kupfersalzes von Salicylaldehyd-4-oxybenzoylhydrazon ist aber deutlich braun. In diesem Falle also könnte sich das Wasser mehr oder weniger an der Koordination beteiligen.

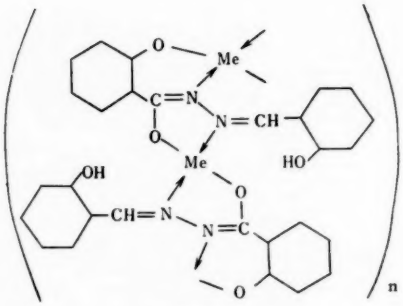
Diese Salze sind alle in Pyridin leicht löslich und können daraus umkristallisiert werden. Die Kupfersalze bilden schwärzlich-braune Kristalle und enthalten an Stelle des Ammoniaks je 1 Mol. Pyridin, das sich beim Erhitzen in Vakuum völlig abspalten lässt. Die pyridinfreien Salze sind olivgrün. Die Nickelsalze bilden zwar bräunlich-rote Kristalle, die aber keine stöchiometrische Menge Pyridin enthalten. Doch ausnahmsweise enthält das Nickelsalz von Salicylaldehyd-2-oxybenzoylhydrazon 3 Mol. Pyridin. Beim Erhitzen in Vakuum werden nur 2 Mol. Pyridin, mit Glanzverlust, aber ohne Farbveränderung der Kristalle abgegeben



VII



VIII



IX

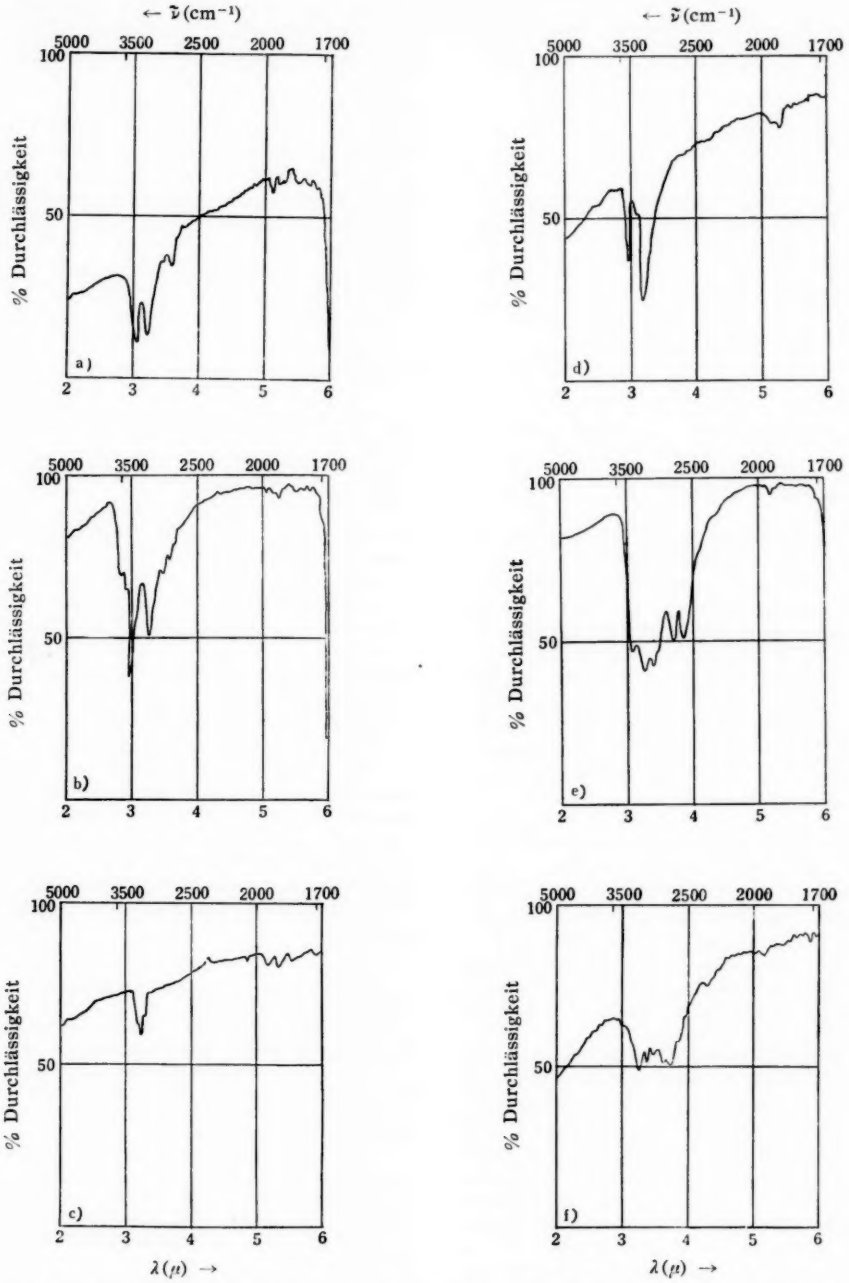


Abb. 2. IR-Spektren. a) Benzaldehyd-benzoylhydrazon; b) Salicylaldehyd-benzoylhydrazon; c) *N*-Salicyliden-*N'*-benzoyl-hydrazino-kupfer(II); d) *N*-Salicyliden-*N'*-benzoyl-hydrazino-monoammin-nickel(II); e) Salicylaldehyd-2-oxybenzoyl-hydrazon; f) *N*-Salicyliden-*N'*-(2-oxybenzoyl)-hydrazino-kupfer(II). (Hexachlorbutadien-Paste).

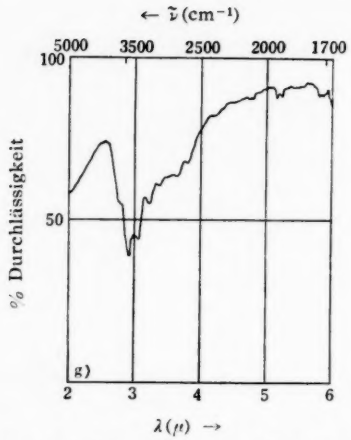


Abb. 2. IR-Spektren. g) *N*-Salicyliden-*N'*-(2-oxybenzoyl)-hydrazino-monoammin-nickel(II). (Hexachlorbutadien-Paste).

(Kristallpyridin); 1 Mol. Pyridin haftet so fest, dass es sich nicht entfernen lässt.

Aus den strukturellen Überlegungen und diesen experimentellen Tatsachen kann man schliessen, dass Ammoniak sowohl als Pyridin (Kristallpyridin ausgenommen) koordinativ mit den Metallatomen gebunden sind, und die Komplexsalze mit VI formuliert werden können. In den ammoniak- bzw. pyridinfreien Kupferkomplexsalzen sind die Kupferatome deshalb koordinativ 3-zählig.

Nach den analytischen Daten allein, könnte man den Komplexsalzen des Salicylaldehyd-2-oxybenzoylhydrazons auch die Formel VII, VIII order IX geben, aber diese drei Formeln werden wohl als unwahrscheinlich ausgeschlossen, weil

1) die hier erhaltenen Komplexsalze schöne Kristalle bilden, während die Salze von der Formel VII, VIII oder IX nur als Pulver erhalten würden,

2) die Ausbildung der Salze von der Formel VIII bzw. IX sterisch nicht oder sehr schwer möglich ist, und schliesslich,

3) die IR-Spektren der Komplexsalze die Anwesenheit chelatisierter Hydroxylgruppen sicher machen; die Salze VII keine Hydroylgruppe, diejenigen von der Formel VIII oder IX nur die nicht chelatisierten Hydroxylgruppen, besitzen sollten.

Einige Vesuche, sie zu methylieren und aus den methylierten Komplexsalzen das Salicylaldehyd-2-methoxybenzoylhydrazon zu isolieren, aber schlugen fehl.

Erhalten wurden, Salicylaldehyd-2-oxy-4-aminobenzoylhydrazon, 5-Bromsalicylaldehyd-2-oxybenzoylhydrazon; *N*-Salicyliden-*N'*-benzoyl-hydrazino-monoammin-kupfer(II)-monohydrat, *N*-Salicyliden-*N'*-benzoyl-hydrazino-monopyridin-kupfer(II), *N*-Salicyliden-*N'*-benzoyl-hydrazino-kupfer-(II), *N*-Salicyliden-*N'*-(2-methoxybenzoyl)-hydrazino-kupfer(II), *N*-Salicyliden-*N'*-(4-oxybenzoyl)-hydrazino-monoammin-kupfer-(II)-monohydrat, *N*-Salicyliden-*N'*-(4-oxybenzoyl)-hydrazino-monoammin-kupfer-(II), *N*-Salicyliden-*N'*-(4-oxybenzoyl)-hydrazino-mono-pyridin-kupfer(II), *N*-Salicyliden-*N'*-(4-oxybenzoyl)-hydrazino-kupfer (II), *N*-Salicyliden-*N'*-(2-oxybenzoyl)-hydrazinomonoammin-kupfer(II)-monohydrat, *N*-Salicyliden-*N'*-(2-oxybenzoyl)-hydrazino-monoammin-kupfer(II), *N*-Salicyliden-*N'*-(2-oxybenzoyl)-hydrazino-monopyridin-kupfer(II), *N*-(5-Bromsalicyliden)-*N'*-(2-oxybenzoyl)-hydrazino-kupfer(II); *N*-Salicyliden-*N'*-benzoyl-hydrazino-monoammin-nickel(II), *N*-Salicyliden-*N'*-(4-oxybenzoyl)-hydrazino-monoammin-nickel(II), *N*-Salicyliden-*N'*-(2-oxybenzoyl)-hydrazino-monoammin-nickel(II), *N*-Salicyliden-*N'*-(2-oxybenzoyl)-hydrazino-monopyridin-nickel(II)-dipyridinat, *N*-Salicyliden-*N'*-(2-oxybenzoyl)-hydrazino-monopyridin-nickel(II), *N*-Salicyliden-*N'*-(2-oxy-4-aminobenzoyl)-hydrazino-monoammin-nickel(II)-monohydrat, *N*-Salicyliden-*N'*-(2-oxy-4-aminobenzoyl)-hydrazino-monoammin-nickel(II), und *N*-(5-Bromsalicyliden)-*N'*-(2-oxybenzoyl)-hydrazino-monoammin-nickel(II).

Beschreibung der Versuche

Die IR-Spektren wurden mit dem Ōyō-Kōken-Gerät, Modell DS 201 aufgenommen.

Salicylaldehyd-aroylhydrazone.—Sie sind, im allgemeinen, durch Gemischen berechneter Mengen von Salicylaldehyd und Säurehydraziden im Alkohol leicht darstellbar.

Salicylaldehyd-2-oxy-4-aminobenzoylhydrazon.—Man mischt 1.2 g Salicylaldehyd in 25 ccm Ammoniakwasser (28%) und 1.7 g 2-Oxy-4-aminobenzoesäurehydrazid in 15 ccm Ammoniakwasser. Nach einiger Zeit neutralisiert man vorsichtig mit verdünnter Salzsäure und kristallisiert den so entstandenen Niederschlag aus wässrigem Pyridin um. Hellgelbe Platten, die bei 225°C zu zersetzen beginnen und bei 259~260°C (unkorr.) unter Zersetzung schmelzen.

Anal. Gef.: C, 62.00; H, 4.84; N, 15.54. Ber. für $C_{14}H_{13}O_3N_3$: C, 61.98; H, 4.83; N, 15.49%.

5 - Bromsalicylaldehyd - 2 - oxybenzoylhydrazon wurde nach der allgemeinen Methode dargestellt und aus Eisessig umkristallisiert. Hellgelbe Nadeln, die bei 271～272°C (unkorr.) unter Zersetzung schmelzen.

Anal. Gef.: C, 49.97; H, 3.49; N, 8.12. Ber. für $C_{14}H_{11}O_3N_2Br$: C, 50.17; H, 3.31; N, 8.36%.

Kupferkomplexsalze. — *N-Salicyliden-N'-benzoyl-hydrazino-monoammin-kupfer(II)-monohydrat.* —Man gibt zur Lösung von 240 mg Salicylaldehydbenzoylhydrazon in 15 ccm Ammoniakwasser(28%)-Alkohol-Gemische (Volumverhältnis: 2:1), 200 mg Kupferacetat (Monohydrat) gelöst in 5 ccm demselben Gemische. Es entsteht sofort eine grüne Lösung, aus der braune Nadeln nach und nach ausfallen.

Anal. Gef.: C, 50.21; H, 4.58; N, 12.33; H_2O+NH_3, 10.34; Cu, 18.62. Ber. für $C_{14}H_{10}O_2N_2 \cdot NH_3 \cdot Cu \cdot H_2O$: C, 49.92; H, 4.49; N, 12.48; H_2O+NH_3, 10.41; Cu, 18.86%.

N-Salicyliden-N'-benzoyl-hydrazino-monopyridin-kupfer(II).—Man fügt zur Lösung von 240 mg Salicylaldehyd-benzoylhydrazon in 10 ccm Alkohol, eine Lösung von 200 mg Kupferacetat (Monohydrat) in 20 ccm Alkohol zu. Es scheidet sich sofort ein gelblich-grüner Niederschlag ab, der aus Pyridin-Wasser-Gemische umkristallisiert wird. Grünlich-braune Säulen oder grünlich-schwarze Körnchen.

Anal. Gef.: C, 60.09; H, 4.02; N, 11.09; Py., 20.50; Cu, 16.81. Ber. für $C_{14}H_{10}O_2N_2 \cdot C_5H_5N \cdot Cu$: C, 59.91; H, 3.97; N, 11.03; Py., 20.77; Cu, 16.68%.

N - Salicyliden - N'-benzoyl - hydrazino - kupfer(II) wird durch 1- bis 2-stündiges Erhitzen vom Ammin-oder Pyridin-Salze unter vermindertem Drucke (130°C/25 mmHg) erhalten. Die Farbe ist olivgrün.

Anal. Gef.: C, 56.14; H, 3.51; N, 9.09; Cu, 20.82. Ber. für $C_{14}H_{10}O_2N_2Cu$: C, 55.72; H, 3.34; N, 9.28; Cu, 21.05%.

N-Salicyliden-N'-(2-methoxybenzoyl)-hydrazino-kupfer(II).—Man versetzt eine Lösung von 166 mg 2-Methoxybenzoesäurehydrazid in 5 ccm Alkohol mit 122 mg Salicylaldehyd. Eine gelbe Lösung entsteht, zu der man eine Lösung von 200 mg Kupferacetat (Monohydrat) in 5 ccm Ammoniakwasser (28%) gibt. Die so erhaltene, schwarzgrüne klare Lösung engt man auf dem Wasserbade allmählich ein. Dunkelgrüne Nädelchen, die in Pyridin so leicht löslich sind, dass sie sich nicht daraus umkristallisieren lassen.

Anal. Gef.: C, 54.26; H, 3.97; N, 8.32; Cu, 19.18. Ber. für $C_{15}H_{12}O_3N_2Cu$: C, 54.30; H, 3.64; N, 8.44; Cu, 19.15%.

N-Salicyliden-N'-(4-oxybenzoyl)-hydrazino-monoammin-kupfer(II)-monohydrat wird in derselben Weise wie beim *N*-Salicyliden-*N'*-(2-methoxybenzoyl)-hydrazino-kupfer(II), aus 256 mg Salicylaldehyd-4-oxybenzoylhydrazon in 10 ccm Ammoniakwasser (28%) und 200 mg Kupferacetat (Monohydrat) in 5 ccm Ammoniakwasser dargestellt. Dunkelgrüne glänzende Nädelchen oder Prismen.

Anal. Gef.: C, 47.72; H, 4.55; N, 11.71; H_2O, 5.19; Cu, 17.98. Ber für $C_{14}H_{10}O_3N_2 \cdot NH_3 \cdot Cu \cdot H_2O$: C, 47.66; H, 4.28; N, 11.91; N_2O, 5.11; Cu, 18.01%.

N-Salicyliden-N'-(4-oxybenzoyl)-hydrazino-monoammin-kupfer(II) wird durch 1-stündiges Erhitzen des Monohydrates auf 110～120°C/25 mmHg erhalten. Schwärzlich-braune, glänzende Kristalle.

Anal. Gef.: C, 49.81; H, 4.32; N, 12.53; NH_3, 4.92; Cu, 19.15. Ber. für $C_{14}H_{10}O_3N_2 \cdot NH_3 \cdot Cu$: C, 50.22; H, 3.91; N, 12.55; NH_3, 5.09; Cu, 18.98%.

N-Salicyliden-N'-(4-oxybenzoyl)-hydrazino-monopyridin-kupfer(II) wird durch Umkristallisieren von den Ammin-Salzen aus Pyridin dargestellt. Schwarz-violette, glänzende Körnchen.

Anal. Gef.: C, 57.95; H, 4.05; N, 10.67; Py., 19.93; Cu, 15.86. Ber. für $C_{14}H_{10}O_3N_2 \cdot C_5H_5N \cdot Cu$: C, 57.50; H, 3.81; N, 10.59; Py., 19.93; Cu, 16.01%.

N - Salicyliden - N' - (4 - oxybenzoyl) - hydrazino-kupfer(II) wird entweder durch 2-stündiges Erhitzen von den Ammin-Salzen auf 160～170°C/25 mm Hg als dunkelgrünes Pulver, oder durch 7-stündiges Erhitzen vom Pyridin-Salze auf 170°C/25 mmHg als gelb-grünes Pulver erhalten.

Anal. Gef.: C, 52.96; H, 3.44; N, 8.81; Cu, 19.58. Ber. für $C_{14}H_{10}O_3N_2Cu$: C, 52.91; H, 3.17; N, 8.82; Cu, 19.99%.

N-Salicyliden-N'-(2-oxybenzoyl)-hydrazino-monoammin-kupfer(II)-monohydrat. — Man fügt zur Lösung von 256 mg Salicylaldehyd-2-oxybenzoylhydrazon in 15 ccm verdünntem Ammoniakwasser (hergestellt aus 1 Vol. 28%-igem Ammoniakwasser und 1 Vol. Wasser), eine Lösung von 200 mg Kupferacetat (Monohydrat) in 10 ccm verdünntem Ammoniakwasser zu. Es fällt sofort ein hellgrüner Niederschlag ab, den man aus Ammoniakwasser-Alkohol-Gemische (Volumverhältnis: 1:2) umkristallisiert. Bräunlich-grüne Nadeln.

Anal. Gef.: C, 47.85; H, 4.39; N, 11.79; H_2O, 5.40; Cu, 18.22. Ber. für $C_{14}H_{10}O_3N_2 \cdot NH_3 \cdot Cu \cdot H_2O$: C, 47.66; H, 4.28; N, 11.91; H_2O, 5.11; Cu, 18.01%. Erhitzt man das Komplexsalz 1 Stunde auf 80～100°C/25 mmHg, so erhält man das kristallwasserfreie Salz, *N-Salicyliden-N'-(2-oxybenzoyl)-hydrazino-monoammin-kupfer(II)*, in bräunlich-grünen Nadeln.

Anal. Gef.: C, 50.71; H, 3.64; N, 10.85; NH_3, 4.70; Cu, 18.72. Ber. für $C_{14}H_{10}O_3N_2 \cdot NH_3 \cdot Cu$: C, 50.22; H, 3.91; N, 12.55; NH_3, 5.09; Cu, 18.98%.

N-Salicyliden-N'-(2-oxybenzoyl)-hydrazino-monopyridin-kupfer(II).—Man kristallisiert den hellgrünen Niederschlag oder die Ammin-Salze aus Pyridin um. Schwarz-grüne Säulen.

Anal. Gef.: C, 57.39; H, 4.05; N, 10.56; Py., 19.93; Cu, 15.96. Ber. für $C_{14}H_{10}N_2O_3 \cdot C_5H_5N \cdot Cu$: C, 57.50; H, 3.81; N, 10.59; Py., 19.93; Cu, 16.01%.

N - Salicyliden - N' - (2 - oxybenzoyl) - hydrazino-kupfer(II).—Man erhält es entweder durch 2-stündiges Erhitzen von den Ammin-Salzen auf 130～140°C/25 mmHg, oder durch 4-stündiges Erhitzen vom Pyridin-Salz auf 130～140°C/25 mmHg als gelb-grünes Pulver.

Anal. Gef.: C, 52.85: H, 3.09; N, 8.76, Cu, 20.11. Ber. für $C_{14}H_{10}O_3N_2Cu$: C, 52.91; H, 3.17; N, 8.82; Cu, 19.99%.

N-Salicyliden-N' - (2 - oxy - 4 - aminobenzoyl) - hydrazino-kupfer(II).—Man gibt zur Lösung von 271 mg Salicylaldehyd-2-oxy-4-aminobenzoylhydrazon in 10 ccm Ammoniakwasser (28%), eine Lösung von 200 mg Kupferacetat (Monohydrat) in 10 ccm Ammoniakwasser. Der anfangs entstandene grüne

Niederschlag wird, während des Umrührens, bräunlich-grüne Nädelchen, die man aus Pyridin umkristallisiert. Schwarz-violette Säulen, die keine stöchiometrische Menge Pyridin enthalten. Analysiert wurde eine Substanzprobe, die durch 2-stündiges Erhitzen auf 130~140°C/25 mmHg als dunkelgrünes Pulver erhalten worden war.

Anal. Gef.: C, 50.76; H, 3.48; N, 12.39; Cu, 18.81. Ber. für $C_{14}H_{11}O_3N_3Cu$: C, 50.53; H, 3.33; N, 12.63; Cu, 19.09%.

N-(5-Bromsalicyliden)-N'-(2-oxybenzoyl)-hydrazino-monoammin-kupfer(II).—Man gibt zur Lösung von 335 mg 5-Bromsalicylaldehyd-2-oxybenzoylhydrazon in 15 ccm *n*-Propylalkohol-Ammoniakwasser (28%)-Gemische (Volumverhältnis: 2:1), eine Lösung von 200 mg Kupferacetat (Monohydrat) in 15 ccm demselben Gemische. Gelb-grüne Nädelchen.

Anal. Gef.: C, 40.48; H, 3.13; N, 9.72; NH_3, 4.26; Cu, 15.30. Ber. für $C_{14}H_9O_3N_2Br \cdot NH_3 \cdot Cu$: C, 40.64; H, 2.92; N, 10.16; NH_3, 4.12; Cu, 15.36%.

N-(5-Bromsalicyliden)-N'-(2-oxybenzoyl)-hydrazino-monopyridin-kupfer(II). — Man gibt zur Lösung von 335 mg 5-Bromsalicylaldehyd-2-oxybenzoylhydrazon in 10 ccm Ammoniakwasser (28%), eine Lösung von 200 mg Kupferacetat (Monohydrat) in 10 ccm Ammoniakwasser. Es scheidet sich sofort ein dunkelgrüner Niederschlag, der aus Pyridin umkristallisiert wird. Schwarze Säulen. Das Pyridin haftet so fest, dass es durch Erhitzen nur schwer (ca. 20 Stunden, auf 150~160°C/25 mmHg) entfernt werden kann.

Anal. Gef.: C, 48.21; H, 3.06; N, 9.00; Py., 16.67; Cu, 13.06. Ber. für $C_{14}H_9O_3N_2Br \cdot C_5H_5N \cdot Cu$: C, 47.96; H, 2.96; N, 8.83; Py., 16.62; Cu 13.35%.

N-(5-Bromsalicyliden)-N'-(2-oxybenzoyl)-hydrazino-kupfer(II) ist entweder aus dem Ammin- oder dem Pyridin-Salze durch Erhitzen unter vermindertem Drucke darstellbar. Gelb-grünes (aus dem Ammin-Salze) oder olivgrünes (aus dem Pyridin-Salze) Pulver.

Anal. Gef.: C, 42.48: H, 2.32; N, 7.19; Cu, 15.97. Ber. für $C_{14}H_9O_3N_2BrCu$: C, 42.39; H, 2.29; N, 7.06; Cu, 16.02%.

Nickelkomplexsalze. — *N-Salicyliden-N'-benzoylhydrazino-monoammin-nickel(II)*. — Man gibt zur Lösung von 240 mg Salicylaldehyd-benzoylhydrazon in 15 ccm Ammoniakwasser (28%)-Alkohol Gemische (Volumverhältnis: 2:1), eine Lösung von 250 mg Nickelacetat (Tetrahydrat) in 5ccm demselben Gemische. Die enstandene tiefrote Lösung engt man auf dem Wasserbade ein. Es scheiden sich nach dem Erkalten schöne, rote Nadeln aus.

Anal. Gef.: C, 53.62; H, 4.24; N, 13.54; Ni, 18.52. Ber. für $C_{14}H_{10}O_2N_2 \cdot NH_3 \cdot Ni$: C, 53.56; H, 4.17; N, 13.38; Ni, 18.70%.

N-Salicyliden-N'-(4-oxybenzoyl)-hydrazino-monoammin-nickel(II) ist in derselben Weise wie beim *N*-Salicyliden-*N'*-benzoylhydrazino-monoammin-nickel(II), aus 256 mg Salicylaldehyd-4-oxybenzoylhydrazon in 10 ccm Ammoniakwasser (28%) und 250 mg Nickelacetat (Tetrahydrat) in 5 ccm Ammoniakwasser darstellbar. Schöne, rote Nädelchen.

Anal. Gef.: C, 50.89: H, 4.19; N, 12.58; Ni, 17.60. Ber. für $C_{14}H_{10}O_3N_2 \cdot NH_3 \cdot Ni$: C, 50.96; H, 3.97; N, 12.73; Ni, 17.79%.

N-Salicyliden-N'-(2-oxybenzoyl)-hydrazino-monoammin-nickel(II).—Man fügt 250 mg Nickelacetat (Tetrahydrat) gelöst in 10 ccm Ammoniakwasser (28%) zu einer Lösung von 256 mg Salicylaldehyd-2-oxybenzoylhydrazon in 100 ccm Ammoniakwasser zu. Das Gemisch trübt sich. Nach einiger Zeit beginnen hellbraune, glänzende Kristalle sich auszuscheiden, die abgesaugt und mit wenig Ammoniakwasser gewaschen werden. Beim Liegen an der Luft schlägt die Farbe von Hellbraun nach Orangerot um. Orangerote, glänzende Blättchen.

Anal. Gef.: C, % 50.75; H, 4.12; N, 12.22; Ni, 17.91. Ber. für $C_{14}H_{10}O_3N_2 \cdot NH_3 \cdot Ni$: C, 50.96; H, 3.97; N, 12.73; Ni, 17.79%.

N-Salicyliden-N'-(2-oxybenzoyl)-hydrazino-monopyridin-nickel(II)-dipyridinat wird durch Umkristallisieren des Ammin-Salzes aus wässrigem Pyridin dargestellt. Gelblich-braunrote, glänzende, Blätter.

Anal. Gef.: C, 63.45; H, 4.65; N, 12.46; Py, 28.49; Ni, 10.89. Ber. für $C_{14}H_{10}O_3N_2 \cdot C_5H_5N \cdot Ni \cdot 2C_5H_5N$: C, 63.30; H, 4.58; N, 12.73; Py., 28.75; Ni, 10.67%.

N-Salicyliden-N'-(2-oxybenzoyl)-hydrazino-monopyridin-nickel(II).—Man erhitzt das Dipyridinat 1 Stunde auf 110°C/25 mmHg. Braun-rote, glanzlose Blätter.

Anal. Gef.: C, 58.29; H, 4.10; N, 10.68; Ni, 15.12. Ber. für $C_{14}H_{10}O_3N_2 \cdot C_5H_5N \cdot Ni$: C, 58.21; H, 3.86; N, 10.72; Ni, 14.97%.

N-Salicyliden-N'-(2-oxy-4-aminobenzoyl)-hydrazino-monoammin-nickel(II)-monohydrat. — Man gibt zur Lösung von 271 mg Salicylaldehyd-2-oxy-4-aminobenzoylhydrazon in 10 ccm Ammoniakwasser (28%), eine Lösung von 250 mg Nickelacetat (Tetrahydrat) in 10 ccm Ammoniakwasser. Es entsteht eine braunrote, klare Lösung, die man auf dem Wasserbade einengt. Braunrote, glänzende Nadeln, die in Ammoniakwasser leicht löslich sind.

Anal. Gef.: C, 46.59; H, 4.60; N, 15.28; H_2O, 5.11; Ni, 16.00. Ber. für $C_{14}H_{11}O_3N_3 \cdot NH_3 \cdot Ni \cdot H_2O$: C, 46.32; H, 4.44; N, 15.43; H_2O, 4.96; Ni, 16.17%. Erhitzt man das Komplexsalz einige Zeit auf 110~120°C/25 mmHg, so erhält man das kristallwasserfreie Salz, *N-Salicyliden-N'-(2-oxy-4-aminobenzoyl)-hydrazino-monoammin-nickel(II)* als braun-rotes Pulver.

Anal. Gef.: C, 48.53; H, 4.09; N, 16.11; Ni, 17.23. Ber. für $C_{14}H_{11}O_3N_3 \cdot NH_3 \cdot Ni$: C, 48.74; H, 4.09; N, 16.24; Ni, 17.02%.

N-(5-Bromsalicyliden)-N'-(2-oxybenzoyl)-hydrazino-nickel(II).—Man gibt zur Lösung von 335 mg 5-Bromsalicylaldehyd-2-oxybenzoylhydrazon in 10 ccm Ammoniakwasser (28%) - Alkohol - Gemische (Volumverhältnis: 1:1), eine Lösung von 250 mg Nickelacetat (Tetrahydrat) in 10 ccm demselben Gemische. Sofort entsteht eine rot-braune Lösung, aus der, beim gelinden Erwärmen auf dem Wasserbade, rötlich-gelbe Nadeln allmählich auskristallisieren.

Anal. Gef.: C, 41.14; H, 3.09; N, 10.36; Ni,

14.43. Ber. für $C_{14}H_9O_3N_2Br \cdot NH_3 \cdot Ni$: C, 41.12; H, 2.96; N, 10.28; Ni, 14.36%.

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Separation of Radioactive Cesium in Biological Materials

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A number of procedures for the separation of low concentrations of radioactive cesium in natural materials have been studied by several workers. When the final radioassay is to be achieved by beta counting, the first problem is the decontamination of natural radioactive elements, rubidium and potassium, the second is the removal of the other fission activities, particularly of the long-lived strontium-90 and cerium-144, and the third is the method of elimination of the bulk of other elements including sodium and potassium.

In the earlier work on the determination of cesium-137 in biological materials[1], the authors adopted the usual method of separation of the alkali elements, that consists in the elimination of the sulfate ion with barium chloride followed by the removal of alkaline earth elements as carbonate and oxalate. Those procedures were supposed to carry down other fission activities, although the loss of cesium in the whole process was proved to be very small as already reported[2]. The bulk of the sodium chloride and a part of the potassium chloride were removed by hydrochloric acid—the ethanol method and the elimination of rubidium and potassium were effectively undertaken by the cesium chloroplatinate precipitation method in an aqueous medium[3].

This method is certainly generally useful and suitable but the first half of the procedure is troublesome when dealing with a large number of samples. The present study deals with the examination of the direct precipitation of cesium with ammonium phosphomolybdate and a simple and rapid separation method for cesium-137 is presented.

Principle.—The method is based on two separations involving the selective precipitation of cesium with ammonium phosphomolybdate in an acid medium and the relative solubilities of the alkali chloroplatinates in water.

Because an excess of phosphate ion which is usually present in the processed solution of food, urine or tissues will interfere with the perfect precipitation of cesium with ammonium phosphomolybdate, it must be previously removed by alkalination to form calcium and magnesium phosphates. In this procedure a partial elimination of other fission activities can be attained. The precipitated cesium ammonium phosphomolybdate is dissolved in ammonium hydroxide and after boiling to expel excess of ammonia, the precipitation with chloroplatinic acid is performed. The precipitate is weighed and mounted for beta counting.

Experimental

Special Reagents.—Ammonium molybdate solution, 10% of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in water; Cesium carrier (CsCl), 10mg. of Cs per ml. of water; Chloroplatinic acid, 10% of $H_2PtCl_6 \cdot 6H_2O$ in water; Salt solutions, containing 20 g. of K^+,

1) N. Yamagata and T. Yamagata, *Japan Analyst (Bunseki Kagaku)*, **7**, 433 (1958).
2) N. Yamagata and T. Yamagata, ibid., **5**, 37 (1956).
3) N. Yamagata and E. Tajima, This Bulletin, **30**, 674 (1957).

Na^+, and Ca^{2+} respectively, 10 g. of Mg^{2+} and 0.2 g. of Fe^{3+} per liter of water.

Radioactive tracers. — ^{137}Cs (carrier-free), Nitrate in nitric acid solution, from the Radiochemical Center, England; ^{89}Sr (carrier-free), Chloride in hydrochloric acid solution from Oak Ridge National Laboratory Batch No. 229A; ^{144}Ce (carrier-free), Nitrate in nitric acid solution from Oak Ridge National Laboratory Batch No. 50; ^{91}Y (carrier-free), Chloride in hydrochloric acid solution from Oak Ridge National Laboratory Batch No. 76.

To make the conditions of precipitation as close as possible to the actual case, a salt solution containing potassium, sodium, calcium, magnesium and ferric ions was prepared. It was considered to possess a similar elementary composition to food, urine or tissues. A proper quantity of the salt solution was used for the tracer experiments.

Conditions of phosphomolybdate precipitation. — As for the conditions of phosphomolybdate precipitation, above all, for interfering substances, the temperature and the composition of precipitate, many investigations have been reported. As far as only the recovery of cesium is concerned, it matters but little what the composition of the phosphomolybdate precipitate is satisfactory except in the case of 42 ml. of bittern. Two grams of oak leaf ash contained 0.232 g. of potassium and 50 ml of urine contained about 0.05 g. of potassium and 0.2 g. of sodium.

TABLE I

PRECIPITATION OF CESIUM WITH AMMONIUM PHOSPHOMOLYBDATE

Total volume of soln., 50 ml.; conc. HNO_3, 2 ml.; H_3PO_4 (as P), 1 mg.; Cs carrier, 2 mg.

Soln.		NH_4 molybdate soln. added (ml.)	Cs pptd. (%)
Salt soln.	5 ml.	0.5	0
〃	〃	1.0	3.6
〃	〃	2.0	96.9
〃	〃	3.0	100.1
〃	〃	5.0	99.6
Oak leaf ash (processed)	2 g.	3.0	98.8
Human urine (processed)	50 ml.	3.0	95.7
Bittern	10 ml.	3.0	99.6
〃	30 ml.	3.0	95.9
〃	42 ml.	3.0	85.6

may be. For this reason, the solution containing the phosphate ion was heated to 50~60°C and then ammonium molybdate solution was added. To determine the minimum volume of ammonium molybdate solution necessary to precipitate cesium completely, an experiment was performed of which the results are shown in Table I. Provided that one mole of P_2O_5 combines with 24 moles of MoO_3, 0.68 ml of 10% ammonium molybdate solution is equivalent to 1 mg. of phosphorus. The result of the experiment indicates that about three times or more excess of the reagent solution is needed for the perfect precipitation of cesium.

Several samples of natural materials were substituted for the salt solution and the result

TABLE II

EFFECT OF SEVERAL IONS ON THE RECOVERY OF CESIUM

Total vol. of soln., 100 ml.; conc. HNO_3, 4 ml.; H_3PO_4 (as P), 2 mg.; ^{137}Cs, carrier-free; NH_4 molybdate soln., 10 ml.

Ions	Concn. (%)	^{137}Cs recovery (%)
NH_4^+ (nitrate)	0	99.2
〃	0.01	98.2
〃	0.1	97.2
〃	1	68.0
〃	5	23.7
K^+ (chloride)	1	99.5
〃	5	87.4
〃	10	79.9
〃	20	53.3
Na^+ (chloride)	1	100
〃	2	98.9
〃	5	99.2
〃	10	98.9

One hundred milliliters of the bittern contained 4.99 g. of potassium chloride, 5.24 g. of sodium chloride, 24.8 g. of magnesium chloride and 8.36 g. of magnesium sulfate and the results of the experiment indicate that milligram quantities of cesium could successfully be precipitated from considerably dense solutions.

Effect of several ions on the recovery of cesium.—The effect of ammonium, potassium and sodium ions on the recovery of carrier-free cesium was examined (Table II). A bulk quantity of those ions which hastened the separation of the precipitate and ammonium ion might decrease the solubility as a result of the common-ion effect. At concentrations above one per cent of ammonium and five per cent of potassium, the precipitate carried no more the cesium tracer completely. Sodium chloride did not interfere with the perfect precipitation at its almost saturated solution.

TABLE III

PRECIPITATION OF VARIOUS AMOUNTS OF CESIUM BY THE PHOSPHOMOLYBDATE METHOD

Total vol. of soln., 100 ml.; conc. HCl, 4 ml.; H_3PO_4 (as P), 2 mg.; NH_4Cl (as NH_4), 100 mg.; Ammonium molybdate soln., 10 ml.; ^{137}Cs activity added, 1750 c.p.m.

Cs taken mg.	Activity carried c. p. m.	Cs recovery %
carrier-free	1718	98.2
0.01	1726	98.6
0.1	1740	99.4
1	1773	101
10	1782	101
100	239	13.6

TABLE IV

CONTAMINATION OF CESIUM AMMONIUM PHOSPHOMOLYBDATE WITH OTHER FISSION ACTIVITIES

Tracer	Carrier	Activity taken c. p. m.	Activity carried c. p. m.	Contamination %	Remarks
^{89}Sr	carrier-free	3.3×10^5	227	0.068	HNO_3 acid
〃	〃	〃	95	0.029	HCl acid
〃	Sr 70 p.p.m.	4.1×10^4	23	0.056	HCl acid
^{144}Ce	carrier-free	5×10^4	80	0.16	HNO_3 acid
〃	〃	〃	86	0.17	HCl acid
^{91}Y	〃	5×10^4	175	0.35	HNO_3 acid
〃	〃	〃	203	0.40	HCl acid

Effect of the amount of carrier cesium.—For the purpose of determining cesium-137 concentrations in natural materials, a definite quantity of carrier cesium is added prior to the separation procedures, and the measured activity must be corrected for the chemical yield of cesium. To determine a preferable amount of the carrier, and to ditermine whether various amounts of cesium could successfully be precipitated with ammonium phosphomolybdate or not, an experiment was carried out. The result is shown in Table III. From tracer concentrations up to 100 p.p.m. of cesium in acid solution could be perfectly precipitated with ammonium phosphomolybdate in the presence of 20 p.p.m. of phosphorus.

Contamination of cesium ammonium phosphomolybdate with other fission activities.—Contamination of cesium ammonium phosphomolybdate with other radioactive nuclides is a matter of concern when a direct precipitation is performed without scavenging pretreatment. Attention has therefore been centered on isotopes of fairly long half-lives, strontium and cerium. Cesium was precipitated from the solution containing each of the following, strontium-89, cerium-144 and yttrium-91, and the precipitate was mounted for counting. The conditions of the precipitation were the same as described in Table I. The result shown in Table IV indicates good decontamination of each of the nuclides in question.

Contamination with potassium and rubidium.—An accurate estimation of cesium-137 by beta counting will be unsuccessful when the precipitate of cesium ammonium phosphomolybdate is contaminated with rubidium and/or potassium. According to the geochemical studies by one of the authors on the rare alkali elements in biological materials[4], the average weight ratio of K : Rb : Cs was about $10^5 : 10^2 : 1$ for natural plants. A preliminary investigation on the cesium-137 concentration indicated that the isotopic ratio of $^{137}Cs : {}^{133}Cs$ in 1957 was $(1\sim10)\times10^{-8}$ for human urine and Japanese food materials. Thus the disintegration ratio of $^{40}K : {}^{87}Rb : {}^{137}Cs$ is calculated to be approximately 200 : 5 : (2～20).

When the radioactivity of cesium-137 is to be measured with an average error of 10% and the contamination with potassium and/or rubidium must be kept less than 2～3% of the cesium activity, a decontamination factor of 10～100 is necessary for rubidium and $10^3\sim10^4$ is necessary for potassium.

TABLE V

CONTAMINATION OF AMMONIUM PHOSPHOMOLYBDATE PRECIPITATE WITH POTASSIUM AND RUBIDIUM

Total vol. of soln., 100 ml.; conc. HNO_3, 4 ml.; H_3PO_4 (as P), 2 mg.; NH_4 molybdate soln., 10 ml.

Dissolved element mg.		Found in ppt. mg.	Decontamination factor
K	0.1	n. d.	—
〃	1	n. d.	—
〃	10	n. d.	—
〃	10^2	0.1	10^3
〃	10^3	1.1	9×10^2
〃	10^4	7.3	1.4×10^3
Rb	0.01	n. d.	—
〃	0.1	n. d.	—
〃	1	0.5	2
〃	10	4.3	2.3
〃	10^2	13	7.7

Ammonium phosphomolybdate was precipitated from the solutions containing various amounts of potassium and rubidium and analyzed for those elements by a flame photometry. The result shown in Table V suggests that this single separation is insufficient for the necessary decontamination especially for rubidium. Another step of decontamination is desirable. To meet with this demand, the chloroplatinate precipitation method[3] was adopted because of the great difference of solubilities between the alkali elements including ammonium. The potassium chloroplatinate is approximately 90 times, the ammonium salt 60 times, and the rubidium salt 3 times more soluble in water than the cesium chloroplatinate at 20°C[3]. This method was already proposed for the carrier-free separation of cesium by one of the authors.

4) N. Yamagata, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **72**, 299, 610 (1951).

TABLE VI
PHOSPHATE ELIMINATION BY HOT-WATER EXTRACTION
(200 ml. of human urine)

No.	^{137}Cs			P	
	added c.p.m.	extracted c.p.m.	recovery %	contained mg.	extracted mg.
1	1920	1816	94.6	816	110
2	1948	1853	95.2	827	112
3	1937	1809	93.5	686	92.5
4	2111	2003	94.8	356	48.0

Preliminary removal of excessive phosphate and other fission activities.—Biological material contains a bulk quantity of phosphate and the phosphomolybdate precipitation can not be applied directly, because an excess of phosphate and a shortage of ammonium molybdate reagent results in insufficient precipitation of cesium as shown in Table I. When sufficient quantity of the reagent for the perfect precipitation of phosphate is added, a bulky precipitate is formed and the later treatment will become impracticable.

Dry-ashed biological material was treated with hydrochloric - nitric acid mixture (1 : 1) and heated to dryness to destroy the remaining organic matter. If organic matter remains, it may interfere with the precipitation of ammonium phosphomolybdate. The completely dried residue was repeatedly extracted with hot water. The recovery of cesium by the hot-water extraction was checked by a tracer experiment and the result was satisfactory (93.5～95.2%). By this means, a greater part of phosphate remained insoluble as calcium or magnesium phosphate (Table VI).

The extract was treated with ammonium hydroxide and the phosphates of calcium and magnesium were precipitated. These carried down the tracers of cerium-144 and yttrium-91 almost perfectly and a part of strontium-89. The loss of cesium-137 was only a tenth of one per cent (Table VII).

TABLE VII
REMOVAL OF THE FISSION ACTIVITIES BY PHOSPHATE PRECIPITATION
Total vol. of soln., 150 ml.; Salt soln., 50 ml.; H_3PO_4 (as P), 100 mg.; conc. NH_4OH, 2 ml. excess.

Tracer (carrier-free)	Activity taken c. p. m.	Activity carried c. p. m.	Removal %
^{89}Sr	39853	6703	16.8
^{91}Y	47501	47401	99.8
^{137}Cs	21573	37	0.17
^{144}Ce	64947	64712	99.6

Over-all decontamination and recovery of cesium.—The elimination of other elements and radioactive nuclides by the present method of cesium separation is schematically summarized in Table VIII. The over-all decontamination and the recovery of cesium were determined by an experiment with 75 ml. of salt solution (containing 1.5 g. each of calcium, potassium and sodium, 0.75 g. of magnesium and 0.015 g. of iron). The solution was diluted to about 300 ml. with water after the addition of 10～30 mg. of cesium carrier, 1 mg. of rubidium and a proper quantity of radioactive tracer. Then, it was treated as described in the following paragraph under separation. The precipitate of cesium chloroplatinate was examined for the presence of ammonium, rubidium, and potassium after being weighed and counted.

TABLE VIII
ELIMINATION OF OTHER ELEMENTS AND NUCLIDES BY THE PRESENT METHOD OF CESIUM SEPARATION

	Procedure	Eliminated elements and nuclides
1st	Phosphate pptn.	Ca, Mg, Fe, Al, Heavy metals ^{144}Ce, ^{91}Y
2nd	NH_4 phosphomolybdate pptn.	Ca, Mg, K, Na ^{144}Ce, ^{89}Sr, ^{91}Y
3rd	Chloroplatinate pptn.	NH_4^+, ^{87}Rb, ^{40}K

Only a trace of ammonium was found in the precipitate. The contribution of the activity of potassium-40 is less than 0.2 dpm, while that of rubidium-87 is calculated as approximately 1 dpm without regard to self absorption. As the beta energy of rubidium-87 is considerably lower (0.275 Mev) than that of cesium-137 (0.52 Mev), the greater absorption minimizes the contribution of contaminated rubidium activity to the cesium activity[1].

A device for cesium-133 determination.—The precipitation of a trace of cesium with ammonium phosphomolybdate is so effective that it can be applied to the determination of natural cesium in biological materials without the addition of a carrier.

The precipitate of cesium ammonium phosphomolybdate is dissolved in ammonium hydroxide. The ammoniacal solution is passed through an anion-exchange resin column (OH-form. For example, ϕ 8 mm.×150 mm., Diaion SA #200). The effluent solution is free from phosphate and molybdate and contains ammonium hydroxide and cesium. The solution is evaporated to expel excess of ammonia and to reduce the volume. After neutralization with a drop of

TABLE IX

OVER-ALL DECONTAMINATION AND RECOVERY OF CESIUM

Cs carrier added mg.	Cs recovery %	Activity added c.p.m.	Activity carried c.p.m.	Decontamination factor	K carried μg	Rb carried μg
10	80.5	—	—	—	93	26
30	93.1	—	—	—	77	20
20 (Sr 1 mg.)	84.8	^{89}Sr 6.6×10^5	2.1	3×10^5	88	13
20	92.7	^{91}Y 9.2×10^5	6.1	1.5×10^5	99	21
20	90.4	^{144}Ce 2.2×10^6	10.2	2×10^5	72	18

hydrochloric acid, the cesium can be determined without interference of any other elements by a flame spectrophotometric technique.

Proposed Procedure

The following procedure is proposed for the determination of cesium-137 in biological materials and soil samples. It has been designed for samples containing approximately 10 μμc of cesium-137 or 1/2~1/7 g. of potassium[5]. An aliquot of the sample must be taken aside before the addition of cesium carrier when the natural cesium-133 is being determined.

Sample Preparation.—*Urine.*—Add 50ml. of nitric acid and 2 ml. of cesium carrier to 500 ml. of urine in a beaker and evaporate to approximately 50 ml. Transfer the solution into a porcelein dish and heat to dryness. Moisten the residue with hydrochloric-nitric acid mixture (1 : 1) and heat to dryness. Repeat the treatment several times to destroy all of the organic matter. Extract the dried residue with five 50 ml. portions of hot-water and filter. Make up the combined filtrate to approximately 300 ml, and proceed as under separation.

Cereals, Vegetables and Dry Milk.—Dry ash about 300~500 g. of cereals (100~200 g. of dried vegetables, 50 g. of dry milk) at 400~450°C. Extract the ash (or carbonized matter) after the addition of 2 ml. of cesium carrier with five 50 ml. portions of hot hydrochloric acid (1 : 10) and filter. Transfer the combined filtrate into a porcelein dish and evaporate to dryness after the addition of 50 ml. of nitric acid. Extract the dried residue with five 50 ml. portions of hot-water and filter. Make up the combined filtrate to approximately 300 ml, and proceed as under separation.

Soil (N-ammonium acetate extraction).—Add 3 liters of N-ammonium acetate solution (pH 7) to 300 g. of fresh soil in a 5 liter beaker. Stand the mixture for 4~5 days with occasional agitation, and then filter the supernatant. Evaporate the filtrate after the addition of 2 ml. of cesium carrier in a porcelein dish to dryness. Moisten the residue with hydrochloric-nitric acid mixture (1 : 1) and heat to dryness. Repeat the treatment several times to destroy all of the organic matter. Extract the dried residue with five 50 ml. portions of hot-water and filter. Make up the combined filtrate to approximately 300 ml, and proceed as under separation.

Separation.—Add ammonium hydroxide dropwise to the solution derived from sample preparation until a dense precipitate of phosphates appears and then add 2 ml. excess of ammonium hydroxide. Allow to settle and test the supernatant liquid for complete precipitation by the addition of ammonium hydroxide. Filter and wash the precipitate with ammonium hydroxide (1 : 100). Combine the wash solution and the filtrate. Discard the precipitate. Add 20 ml. of nitric acid and 5 mg. of P (as phosphoric acid). Heat the mixture to 50~60°C, then add 20 ml. of 10% ammonium molybdate solution. Agitate vigorously and rub the wall of the beaker with a glass rod to hasten the precipitation. Allow to settle and after cooling filter and wash with 5 portions of nitric acid (2 : 100). Take up the yellow precipitate with ammonium hydroxide (1 : 1) and wash thoroughly with water. Boil the combined filtrate and washings until the odour of ammonia disappears. Dilute to 100 ml. with distilled water and cool with cold water. Add 1 ml. of 10% chloroplatinic acid with stirring. Rub the wall of the beaker with a glass rod until yellow precipitate appears. Stand for several hours. Filter through a weighed one inch filter paper mounted on a Hirsch funnel. Wash with 10 ml. of cold water and 3 portions of ethyl alcohol. Dry the filter paper and precipitate at 110°C and

5) During 1956~57, milk, rice and human urine in different countries showed a general ^{137}Cs concentration of 20~70 μμc ^{137}Cs/g potassium. (U. N. Scientific Committee on the Effects of Atomic Radiation. A/AC.82/R. 65/Add.3 p. 31, 8 May 1958).

weigh to determine the cesium recovery. Mount the precipitate in a measuring dish for counting. Standardize the counter with a known amount of cesium-137 and 20 mg. of cesium carrier precipitated as the chloroplatinate.

Summary

A simple and rapid separation method for cesium-137 in biological materials has been presented. It is composed of three steps, phosphate elimination, ammonium phosphomolybdate precipitation and chloroplatinate precipitation. The over-all yield of cesium is over 85% and the decontamination from other fission activities is more than 10^5 for cerium-144 and strontium-89. The contribution of the activities of rubidium-87 and potassium-40 is negligibly small in the determination of cesium-137 in biological materials by beta counting.

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*The Formation of Coprostane, 6β-Coprostanol, and 3α,6β-Coprostanediol by the Catalytic Reduction of Epicholesterol β-Oxide**

By Yoshiyuki URUSHIBARA and Kazuko MORI

(Received July 22, 1958)

M. Shiota and one of the authors (K. M.)[1] have previously reported on the reduction of epicholesterol β-oxide with lithium aluminum hydride and with sodium and amyl alcohol. In continuation, the present authors have examined the catalytic reduction of epicholesterol β-oxide (I) with Adams platinum oxide, and obtained coprostane (II), 6β-coprostanol (IIIa), and 3α,6β-coprostanediol (VIa). The 3,6-coprostanediol hitherto known being only the 3β,6β-isomer[2], the authors synthesized the 3α,6β-isomer by another method, and confirmed its structure.

Plattner et al.[3] reduced epicholesterol β-oxide with platinum oxide as the catalyst and obtained 3α-cholestanol besides an oily substance supposed to be a hydrocarbon. The present authors, however, obtained coprostane derivatives only, but no cholestane derivatives.

The products from the catalytic reduction of epicholesterol β-oxide (I) with platinum oxide were acetylated, and a chromatographical separation gave coprostane (II), 6β-coprostanol acetate (IIIb), and 3α,6β-coprostanediol diacetate (VIb). The structure of 6β-coprostanol acetate (IIIb) was determined by hydrolyzing the acetate to the free alcohol, 6β-coprostanol (IIIa), oxidizing the alcohol to the corresponding ketone, 6-coprostanone (IV), and isomerizing the latter to 6-cholestanone (V) by treatment with concentrated hydrochloric acid in acetic acid. The β-configuration of the 6-hydroxyl group comes from the β-configuration of the oxide ring of the starting material, epicholesterol β-oxide. The 6β-coprostanol acetate (IIIb) was also identical with the specimen obtained from 4-cholestene-6β-ol acetate by the method of Shoppee et al.[4].

Hydrolysis of 3α,6β-coprostanediol diacetate (VIb) and oxidation of the free diol (VIa) gave 3,6-coprostanedione (VII). The 3α,6β-coprostanediol diacetate synthesized by another method as described below was identical with the 3α,6β-coprostanediol diacetate (VIb) obtained from the catalytic reduction of epicholesterol β-oxide, and probably with the 3α,6β-coprostanediol diacetate prepared by Shoppee

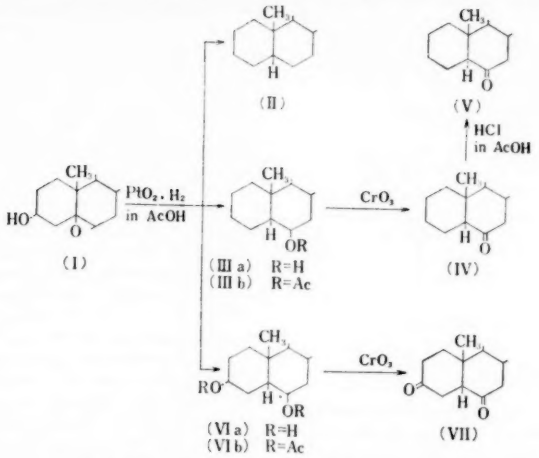
* Presented at the 8th Annual Meeting of the Chemical Society of Japan held in Tokyo, April, 1955, and at the 9th Annual Meeting of the Chemical Society of Japan held in Kyoto, April, 1956.

1) M. Shiota and K. Mori, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **76**, 1192 (1955).

2) V. Prelog and E. Tagmann, *Helv. Chim. Acta*, **27**, 1880 (1944).

3) Pl. A. Plattner, A. Fürst, F. Koller and H. H. Kuhn, ibid., **37**, 258 (1954).

4) D. N. Jones, J. R. Lewis, C. W. Shoppee and G. H. R. Summers, *J. Chem. Soc.*, **1955**, 2876.



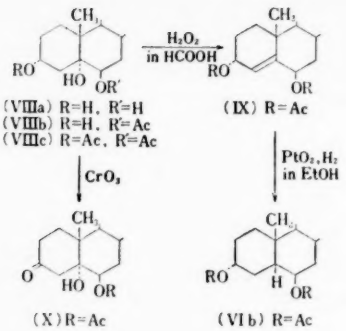
et al.[5] by the reduction of 6β-acetoxy-3-coprostanone followed by acetylation.

Thus it was concluded that the catalytic reduction of epicholesterol β-oxide (I) gave coprostane (II), 6β-coprostanol (IIIa), and 3α,6β-coprostanediol (VIa):

The catalytic reduction of cholesteryl acetate β-oxide with platinum oxide gave cholestane, 3β-cholestanol acetate, and 3β, 6β-cholestanediol 3-acetate but no coprostane derivatives[6,7]. Hence, the formation of the coprostane derivatives in the catalytic reduction of epicholesterol β-oxid may be caused by the effect of the α-configuration of the 3-substituent. Because the 3α-substituent in epicholesterol β-oxide possesses the axial conformation, it may be possible for it to compel the β-face, rather than the normally more easily adsorbed α-face, of the steroid molecule to be adsorbed on the surface of the catalyst, and the subsequent transfer of hydrogen will lead to the formation of coprostane derivatives. Shoppee et al.[8] observed a similar effect of the 3α-substituents on the catalytic reduction of Δ^5-steroids; however, they obtained, besides 3α-coprostanol, about 40% yield of 3α-cholestanol in the case of epicholesterol, and an exclusive yield of coprostane derivatives when the 3α-substituents were greater than the hydroxyl group. The catalytic reduction of epichlesterol β-oxide by the present authors yielded no cholestane derivatives. Shiota et al.[9] observed recently a similar effect of the 3α-substituent on the catalytic reduction of epicholesteryl chloride.

3α,6β-Coprostanediol diacetate (VIb) was synthesized by another route as follows: Treatment of epicholesterol with formic acid and hydrogen peroxide, followed by hydrolysis, acetylation and chromatographic separation, gave 3α,5,6β-cholestanetriol 3,6-diacetate (VIIIc), 3α,5,6β-cholestanetriol 6-acetate (VIIIb), and 3α, 5,6β-cholestanetriol (VIIIa). The structure of 3α,5,6β-cholestanetriol 6-acetate (VIIIb) was determined by oxidizing the 6-acetate to 5,6β-cholestanediol-3-one 6-acetate (X)[10]. 3α,5,6β-Cholestanetriol 3,6-diacetate (VIIIc) and 3α,5,6β-cholestanetriol 6-acetate (VIIIb) are probably identical with the substances obtained by the hydration of epicholesterol α-oxide and β-oxide by Plattner et al.[3]. The authors presume that 3α,5,6β-cholestanetriol 6-acetate (VIIIb) and 3α,5,6β-cholestanetriol (VIIIa) were produced by the hydrolysis of the primary product, 3α, 5,6β-cholestanetriol 3,6-diacetate (VIIIc), on aluminum oxide in chromatographic separation. The 3α,5,6β-cholestanetriol 3,6-diacetate (VIIIc) was dehydrated to 4-cholestene-3α,6β-diol diacetate (IX), and catalytic reduction of the latter gave 3α, 6β-coprostanediol diacetate (VIb), which was identical with the specimen from the catalytic reduction of epicholesterol β-oxide.

5) C. W. Shoppee, R. J. Bridgwater, D. N. Jones and G. H. R. Summers, ibid., **1956**, 2492.
6) M. Chuman, *J. Chem. Soc. Japan, Pure Chem. Soc.* (*Nippon Kagaku Zassi*), **64**, 1486 (1943); Y. Urushibara and M. Chuman, This Bulletin, **22**, 69 (1949).
7) Pl. A. Plattner, Th. Petrzilk and W. Lang, *Helv. Chim. Acta*, **27**, 513 (1944).
8) J. R. Lewis and C. W. Shoppee, *J. Chem. Soc.*, **1955**, 1365.
9) M. Shiota, Y. Kita and T. Sano, Presented at the 11th Annual Meeting of the Chemical Society of Japan held in Tokyo, April, 1958.
10) B. Ellis and V. Petrow, *J. Chem. Soc.*, **1939**, 1078.



(VIIIa) R=H, R'=H
(VIIIb) R=H, R'=Ac
(VIIIc) R=Ac, R'=Ac

(IX) R=Ac

(X) R=Ac

(VIb) R=Ac

Experimental**

Catalytic Reduction of Epicholesterol β-oxide (I). — A suspension of epicholesterol β-oxide (I) (180 mg.) in acetic acid (18 cc.) was shaken with hydrogen in the presence of Adams platinum oxide (36 mg.) at the ordinary temperature and pressure. The reaction was completed in one hour, one mole and a half of hydrogen being absorbed. Evaporation of acetic acid under a reduced pressure from the solution filtered from the catalyst gave an oily substance (178 mg.). Acetylation of the oil with acetic anhydride and pyridine gave an oily substance (183 mg.). It was chromatographed on a column of aluminum oxide (9 g.) prepared in petroleum ether. Elution with petroleum ether (40 cc.) gave an oily material (13.5 mg.), which was brought to crystallization by dissolving it in methanol and placing the solution in a refrigerator. Recrystallization from acetone gave coprostane (II) in needles, m. p. and mixed m. p. 67~70°C.

Elution with petroleum ether-benzene (9 : 1, 60 cc.) gave another material (27 mg.) which on recrystallization from methanol gave a crystalline product (24 mg.), m. p. 108~109°C. It was identified with 6β-coprostanol acetate (IIIb) as follows. It was dissolved in anhydrous ether (1 cc.), the solution was dropped into a solution of lithium aluminum hydride (10 mg.) in anhydrous ether (1 cc.), and the mixture was boiled under a reflux condenser for one hour. The ethereal solution, after being washed and dried, was evaporated to give an oily substance (19.5 mg.). The substance (6β-coprostanol, IIIa) did not crystallize even when placed in a refrigerator in methanol solution, as it did not in the case of Shoppee et al.[4]. The substance was dissolved in acetic acid (0.2cc.) and the solution was mixed with a solution of chromic anhydride (12.5 mg.) in 90% acetic acid (0.5 cc.). After the mixture was left to stand overnight, a small amount of water was added, when crystals (15 mg.), m. p. 125~131°C, were obtained, which were recrystallized from methanol to yield 6-coprostanone (IV) (12 mg.), m. p. 128~129.5°C. The substance (8 mg.) was dissolved in acetic acid (1 cc.) and the solution was refluxed for 30 minutes after adding one drop of concentrated hydrochloric acid. The product (7 mg.) thus obtained was recrystallized from methanol to give 6-cholestanone (V) (5 mg.), m. p. and mixed m. p. 85°C.

The 6β-coprostanol acetate (IIIb) showed no depression of the m. p. in admixture with 6β-coprostanol acetate prepared by the catalytic reduction of 4-cholestene-6β-ol acetate[4].

Fractions (21.5 mg. in total) eluted with benzene-ether (19 : 1, 60 cc.; 9 : 1, 40 cc.) were combined and brought to crystallization by keeping them in a refrigerator in methanol solution. Repeated recrystallization from methanol gave 3α, 6β-coprostanediol diacetate (VIb) (6.5 mg.) in needles, m. p. 103~106.5°C. The substance showed no depression of the m. p. in admixture with the 3α, 6β-coprostanediol diacetate prepared by the catalytic reduction of 4-cholestene-3α, 6β-diol diacetate as described below, but a depression of the m. p. with 3α, 6β-cholestanediol diacetate. Deacetylation of the 3α, 6β-coprostanediol diacetate (VIb) with lithium aluminum hydride gave free 3α, 6β-coprostanediol (VIa) in a glassy mass, m. p. 134~136°C. Oxidation of the latter with chromic anhydride in acetic acid gave 3, 6-coprostanedione (VII) in needles, m. p. 174~175.5°C, which showed no depression of the m. p. on admixture with an authentic specimen of 3, 6-coprostanedione prepared by the oxidation of 3β, 6β-coprostanediol[2], but a depression with 3, 6-cholestanedione.

3α, 5, 6β-Cholestanetriol 3, 6-diacetate (VIIIc).—A suspension of epicholesterol (1 g.) in 90% formic acid (10 cc.) was heated to 70~80°C with stirring for 5 minutes to form the 3-formate which separated in an oily layer, and the mixture was cooled to 25°C. The solidified 3-formate was shaken occasionally with 30% hydrogen peroxide (1 cc.), the temperature being kept at 40°C. In about 30 minutes the solid dissolved and the solution was allowed to stand overnight at room temperature. The mixture was treated with boiling water (15 cc.), and allowed to cool. The white granular solid material was collected, and dissolved in methanol (30 cc.), and the solution was treated with 25% aqueous sodium hydroxide (1 cc.), warmed on the water-bath for 10 minutes, acidified with hydrochloric acid, diluted with water, and extracted with ether. Isolation in the usual way gave 3α, 5, 6β-cholestanetriol (VIIIa) in a glassy mass. Acetylation of the 3α, 5, 6β-cholestanetriol (VIIIa) with acetic anhydride (7 cc.) and pyridine (10 cc.) gave an oily substance (1.2 g.).

This substance was chromatographed on a column of aluminum oxide (30 g.) prepared in petroleum ether. Fractions (450 mg. in total) eluted with petroleum ether-benzene (9 : 1, 2100 cc.; 4 : 1, 2300 cc.) were combined and recrystallized from methanol to give 3α, 5, 6β-cholestanetriol 3, 6-diacetate (VIIIc) (270 mg.), m. p. 86~87°C.

Fractions (190 mg. in total) eluted with petroleum ether-benzene (1 : 1, 300 cc.), benzene (400 cc.) and benzene-ether (99 : 1, 100 cc.; 98 : 2, 100 cc.; 95 : 5, 100 cc.) showed no sharp melting point. The substance is presumed to be a mixture of

** Melting points are uncorrected.

3α, 5, 6β-cholestanetriol 3, 6-diacetate (VIIIc) and 3α, 5, 6β-cholestanetriol 6-acetate (VIIIb), because it gave 3α, 5, 6β-cholestanetriol 3, 6-diacetate (VIIIc) on acetylation.

Fractions (165 mg. in total) eluted with benzene-ether (9 : 1, 200 cc.; 4 : 1, 200 cc.; 1 : 1, 100 cc.) and ether (600 cc.) were recrystallized from methanol to give 3α, 5, 6β-cholestanetriol 6-acetate (VIIIb) (125 mg.), m. p. 177~178°C. The structure of this compound was determined by oxidizing it to a product, m. p. 159~160°C, which showed no depression of the m. p. on admixture with the 5, 6β-cholestanediol-3-one 6-acetate (X), m. p. 163~164°C, prepared by oxidation of 3β, 5, 6β-choletanetriol 6-acetate.

Fractions (170 mg. in total) eluted with ether-acetone (600 cc.) were a gel. The substance is presumed to be a mixture of 3α, 5, 6β-cholestanetriol 6-acetate (VIIIb) and 3α, 5, 6β-cholestriol (VIIIa), for on acetylation it gave 3α, 5, 6β-cholestanetriol 3, 6-diacetate (VIIIc).

4-Cholestene-3α, 6β-diol diacetate (IX).— 3α, 5, 6β-Cholestanetriol 3, 6-diacetate (VIIIc) (165 mg.) was treated with thionyl chloride (2 drops) in pyridine (1 cc.) at 0°C. After 5 minutes the mixture was poured into ice water. Working up in the usual way, it gave a substance and recrystallization from methanol gave 4-cholestene-3α, 6β-diol diacetate (IX) (130 mg.) in needles, m. p. 102.5~103.5°C; $[\alpha]_D^{30}$ +117° (c, 2.20 in chloroform).

Anal. Found: C, 76.30; H, 10.59. Calcd. for $C_{31}H_{50}O_4$: C, 76.50; H, 10.36%.

3α, 6β-Coprostanediol diacetate (VIb).— Platinum oxide (10 mg.) in ethanol (50 cc.) was saturated with hydrogen, and 4-cholestene-3α, 6β-diol diacetate (IX) (47 mg.) was added, and the mixture was shaken with hydrogen at the ordinary temperature and pressure. The reaction was completed in 20 minutes, about one mole of hydrogen being absorbed. Evaporation of ethanol from the filtered solution gave an oil (46 mg.). It was chromatographed on a column of aluminum oxide (1.5 g.) prepared in petroleum ether. Fractions (23 mg. in total) eluted with petroleum ether-benzene (4 : 1, 30 cc.; 7 : 3, 20 cc.; 1 : 1, 20 cc.) were recrystallized from methanol to give 3α, 6β-coprostanediol diacetate (VIb) (18 mg.), m. p. 103~104°C; $[\alpha]_D^{18}$ +56° (c, 1.85 in chloroform).

Anal. Found: C, 76.07; H, 10.79. Calcd. for $C_{31}H_{52}O_4$: C, 76.18; H, 10.72%.

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Electron Diffraction Investigation on the Molecular Structure of 1, 1, 2, 2-Tetrafluoro-1, 2-dichloroethane

By Machio IWASAKI

(Received July 19, 1958)

The molecular structure of some fluorochloroethanes presents two interesting problems. One of them is concerned with rotational isomerism, while the other with the effect of the neighboring halogene atoms on the C–F and C–Cl bond distances. In a previous publication[1], the molecular structure of 1, 2-difluoro-1, 1, 2, 2-tetrachloroethane has been reported. This report presents the results of the determination of the molecular structure of 1,1,2,2-tetrafluoro-1,2-dichloroethane which was undertaken by the sector-microphotometer method of electron diffraction in order to find the effect of substitution with fluorine on the energy difference between isomers and on the bond distances.

The preliminary work[2] on this molecule was carried out merely by the radial distribution method on the assumption of a rather short distance of the C–C bond, 1.46 Å, which had been reported in early investigations on some fluorocarbons[3]. Now, new experimental data obtained by use of an s^3-sector have been analysed by the correlation method as well as the radial distribution method without making any assumption about the C–C bond distance.

Experimental

The sample was prepared by Nagase in this laboratory from hexachloroethane, which was

1) M. Iwasaki, S. Nagase and R. Kojima, This Bulletin, **30**, 230 (1957).

2) M. Iwasaki, S. Nagase and R. Kojima, *J. Chem. Phys.*, **22**, 959 (1954).

3) See Table VII.

fluorinated with antimony trifluoride under a superatmospheric pressure in the presence of antimony pentachloride as a catalyst[4]. The product distilled at 3.8°C. The purity of this sample was tested with an infrared absorption spectrum. It was confirmed that the amount of $CFCl_2$-CF_3, that could not be removed by fractionation, was less than about 1~2 per cent. Hence, its amount was so small as to affect the electron diffraction patterns in an inappreciable manner.

The diffraction patterns were obtained at a room temperature of about 10°C with an apparatus[5] having an r^3-sector, which was rapidly rotated during exposures. The apparatus used was essentially similar to that constructed by Ino[6]. The details will be reported elsewhere. Two nozzle-to-plate distances of 125 mm. and 285 mm. were used: the former was used for large-angle scattering while the latter for small-angle scattering. The extraneous scatterings were prevented by a beam trap fixed at the center of the sector. The wavelength of the electron beam was determined from the Debye rings of a gold foil to be about 0.055 Å. The sample was introduced into the electron beam through a fine nozzle which was surrounded by a trap cooled with liquid air to prevent the sample from spreading throughout the camera chamber. Diffration photographs were taken on Fuji Process Hard Plates with the consecutive exposures of 30~60 sec. The photographic densities were measured up to a q value of about 100 by a Riken B-type recording microphotometer. In this measuremens, the photographic plate was rapidly rotated about the center of the diffraction pattern in order to average out the inevitable irregularities in the emulsion. The microphotometer traces thus obtained were measured by a coordinate comparator as a function of q. After calibrating the non-linearity of voltage-deflection relation of the electrometer in the microphotometer, the photographic density was converted into the relative intensity by the method similar to that employed by J. Karle and his coworker[7].

The molecular scattering intensity, I_m, was calculated from the total scattering, I_t, and a smooth background, I_b, that was drawn with the aid of the positivity criteria[7] as

$$I_m = I_t/I_b - 1 \qquad (1)$$

The averaged molecular scattering intensity qI_m shown by the top curve in Fig. 4 and Fig. 5 was obtained from several photographs with an average deviation of 4 per cent. of maximum amplitude, and it had an index of resolution of 0.95 to 1.00; that is, the ratio of the amplitude of the molecular scattering terms to the magnitude of the smooth background upon which the molecular terms are superposed is 0.95 to 1.00 times that given by theory for a perfect pattern.

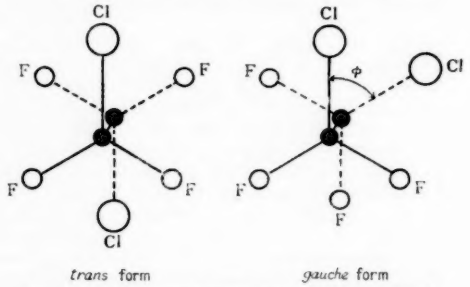

Fig. 1. Stable configurations of CF_2Cl-CF_2Cl.

Analysis

Radial Distribution Curve.—The radial distribution (RD) curve shown in Fig. 2 was calculated by the following equation:

$$f(r) = \sum_{q=0}^{q_{max}} qI_m \exp(-aq^2)\sin(\pi qr/10) \qquad (2)$$

where I_m is the molecular scattering intensity. The artificial damping factor a was chosen so as $\exp(-aq^2) = 0.1$ at $q = 100$, and $q = (40/\lambda)\sin(\theta/2)$, where θ is the angle of scattering and λ is the wavelength of the electron beam.

In the calculation of the RD curves, a theoretical intensity curve with constant coefficients which was computed for the assumed model was substituted in place of the observed intensity below $q = 18$. Several steps of successive approximations were taken in order to make the assumed model selfconsistent with the final RD curve which would satisfy Karle's criteria[7] as closely as possible.

The RD curve has maxima at 1.33_0, 1.74_5, 2.1—3.1, 3.48, 3.90 and 4.29 Å. The first two peaks at 1.33_0 and 1.74_5 Å are assigned to C—F and C—Cl bond distances, respectively. The unresolved peak at 2.1—3.1 Å is due to the superposition of various non-bonded distances, while that at 3.48 Å to the *trans* F···F distance.

There are two conceivable configurations, i. e., the *trans* (C_{2h}) and the *gauche* (C_2) form, for this molecule as shown in Fig. 1. The peak at 3.90 Å corresponds to the *trans* F···Cl distance, which is characteristic of the *gauche* form, while the peak at 4.29 Å corresponds to the *trans* Cl···Cl distance which is characteristic of the *trans* form (see Fig. 1). Therefore, these two peaks evidently show the existence of two isomeric forms for this

4) R. Kojima, M. Iwasaki, S. Nagase and H. Baba, *Repts. Govt. Ind. Research Inst., Nagoya* (*Nagoya Kogyo Gijutsu Shikenjo Hokoku*).**5**, 225 (1956).
5) Y. Morino, M. Kimura and M. Iwasaki, Lectured at the Sixth Annual Meeting of the Chemical Society of Japan, April 1953.
6) T. Ino, *J. Phys. Soc. Japan*, **8**, 92 (1953).
7) J. Karle and I. L. Karle, *J. Chem. Phys.*, **18**, 957 (1950).

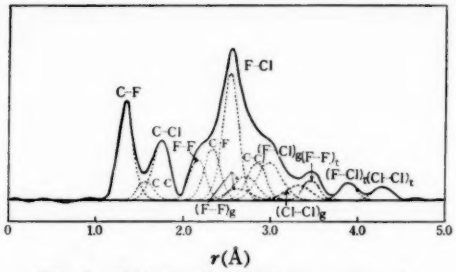

Fig. 2. Radial distribution curve for CF_2Cl-CF_2Cl (the full line). The dotted curves indicate individual peaks for the respective interatomic distances.

molecule. As the area under the RD peak is approximately proportional to Z_iZ_j/r_{ij}, the ratio of the two forms, N_t/N_g, can be calculated from the areas of the two peaks mentioned above by means of the following formula:

$$\frac{N_t}{N_g}=\frac{2Z_F r_{Cl\cdots Cl}A_{Cl\cdots Cl}}{Z_{Cl}r_{F\cdots Cl}A_{F\cdots Cl}} \qquad (3)$$

where Z_F and Z_{Cl} are the atomic numbers of fluorine and chlorine, $A_{Cl\cdots Cl}$ and $A_{F\cdots Cl}$ are the areas of the peaks, and $r_{Cl\cdots Cl}$ and $r_{F\cdots Cl}$ are *trans* Cl···Cl and *trans* F···Cl distances, respectively.

TABLE I

THE ASSUMED AND THE CALCULATED AMOUNT OF THE *GAUCHE* FORM IN ANALYSING THE RD CURVE

Assumed amount of the *gauche* form (%)	Calcd. amount of the *gauche* form (%)
60	54
50	49
45	46
35	42

In applying this formula, it was necessary to use the following procedure. Because the theoretical intensity with constant coefficients was used in place of the observed intensity below $q=18$ in the calculation of the RD curve, the ratio of the areas was affected by the assumed value of the abundance ratio of the two isomers. In order to see this effect, the RD curves were calculated on the assumption that the amount of the *gauche* form is equal to 60, 50, 45 and 35 per cent. The amount of the *gauche* form obtained from the areas of the RD peaks is shown in Table I for various cases. Table I shows that the self-consistent value was obtained from the RD curve if the amount of the *gauche* form was assumed to be equal to 50~45 per cent. Therefore, the amount of the *gauche* form was estimated as 50~45 per cent. from the RD curve. This value was further tested by the consideration of the theoretical intensity curves described in the next section.

In the range from 1.0 to 2.0 Å of the RD curve, a small peak corresponding to the C—C distance is masked by the skirts of prominent peaks on either side of the C—C peak. It seems to be unlikely that the contribution from the C—C distance affects the left side of the C—F peak as well as the right side of the C—Cl peak. Hence the right side of the former peak and the left side of the latter were fitted with Gaussian functions. The Gaussian curves which were fitted almost exactly to each side of the composite peak were subtracted from the composite peak. The remaining area formed a smooth curve having a maximum at 1.54 Å which was attributable to the C—C distance. The three components of the first peak of the RD curve are illustrated in Fig. 2. The areas of these decomposed peaks can favorably be compared with the theoretical values and fairly good agreement was obtained as shown in Table II.

TABLE II

THE RESULT OF ANALYSIS OF THE RD CURVE (THE REGION OF THE BONDED DISTANCES)

		C-F (Å)	C-C (Å)	C-Cl (Å)
Distance		1.33_0	1.54	1.74_5
Mean amplitude	obs.	0.052	0.045	0.061
	calc.	0.045	0.050	0.054
Peak area	obs.	1.00	0.18	0.70
	calc.	1.00	0.14	0.72

The portion of the RD curve from 2.1 to 3.7 Å corresponds to the superposition of the contributions from twelve interatomic distances in the *trans* as well as in the *gauche* form. This part of the RD curve was so complicated that the values of mean amplitudes and the peak heights could not be taken as unknown parameters in decomposing this part; hence the assumed values listed in Table II were used for the mean amplitudes, while for the peak heights the theoretical values calculated from the atomic numbers and the mean amplitudes were used. The amount of the *gauche* form was assumed to be 50 per cent. in accordance with the result obtained from the areas under peaks at 3.90 Å and 4.29 Å. As the left

side of this peak (2.0~2.4 Å) was composed of the contribution from the non-bonded F···F, C···F and F···Cl distances, these three distances were determined from the analysis of this part of the RD curve by trial and error on the assumption described above. The region from 2.4 Å to 3.0 Å was decomposed in a similar manner into contributions from non-bonded C···Cl, *gauche* F···F and *gauche* F···Cl distances. The remaining portion of the RD curve from 3.0 Å to 3.7 Å which was obtained by subtracting the contributions from the distances below 3 Å was, further, decomposed into contributions from the *gauche* Cl···Cl and *trans* F···F distances. These components lying between 2.0 and 3.7 Å are illustrated in Fig. 2. The molecular model which was constructed so as to satisfy the positions of the decomposed peaks as closely as possible, gave the set of interatomic distances listed in Table III. These interatomic distances are in good agreement with the respective RD peaks within 0.01~0.02 Å. Moreover, the azimuthal angle of two C—Cl bonds of the *gauche* form can be estimated to be 62° from the *gauche* Cl···Cl distance. Although the amount of the *gauche* form was fixed at 50 per cent. in the foregoing analysis, the RD curve was affected, as mentioned above, by the assumed value of the abundance ratio of the isomers in the region for r larger than 2.7 Å. In order to see this effect, a number of theoretical and experimental RD curves were computed for various values of the abundance ratio as shown in Fig. 3. The theoretical RD curve shifts gradually from the full line to the dotted one with varying amounts of the *gauche* form from 30 to 70 per cent. On the other hand, the experimental RD curve falls in the shaded portion even if the assumed amounts of the *gauche* form were varied from 30 to 70 per cent. in calculating the theoretical part of the intensity. The discrepancy between the observed and the theoretical RD curve was minimized, when the amount of the *gauche* form was assumed to be about 50 per cent. This fact coincides with the results obtained from the areas of 3.90 and 4.29 Å peaks.

The mean amplitudes listed in Tables II and III were obtained by fitting the RD peaks with Gaussian functions, no corrections being made for second order effects, such as a sample spread, multiple scatterings and the failure of Born approximation[8]. The observed mean amplitudes are

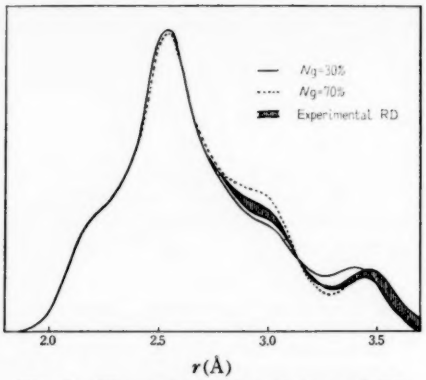

Fig. 3. Theoretical and experimental RD curves. The full line indicates the theoretical RD curve for the amount of the *gauche* form of 30%, and the dotted line for that of 70%. The shaded portion indicates the experimental RD curve, assuming the amount of the *gauche* form ranging from 30 to 70%.

in good agreement with those calculated by Morino et al.[9] from spectroscopic data.

Theoretical Intensity Curves. — The theoretical expression of the molecular scattering intensity obtained experimentally from Eq. 1 is given by the following equation:

$$qI_m(q) = \sum_{i \neq j}\sum (c_{ij}/r_{ij}) \exp(-b_{ij}q^2) \times \sin(\pi q r_{ij}/10) \qquad (4)$$

where r_{ij} denotes the interatomic distance between the i-th and the j-th atom and b_{ij} is the respective temperature factor which is calculated from its mean amplitude listed in Tables II and III. In the region of moderate and large q values, c_{ij} was considered to be constant proportional to Z_iZ_j, while in the region of small q,

$$c_{ij} = (Z_i - f_i)(Z_j - f_j)/\sum (Z_i - f_i)^2 + S_i \qquad (5)$$

was used, where Z_i is the atomic number, and f_i and S_i are the elastic and inelastic atomic scattering factors, respectively. The summations of Eq. 4 were performed by use of punchedcards and a Remington Rand Type-285 Model-2 tabulating machine[10,11]. Though the majority of the

8) R. Glauber and V. Schomaker, *Phys. Rev.*, **89**, 667 (1953); L. S. Bartell and L. O. Brockway, *Nature*, **171**, 978 (1953); J. A. Ibers and J. A. Hoerni, *Acta Cryst.*, **7**, 405 (1954).

9) Y. Morino, K. Kuchitsu, A. Takahashi and K. Maeda, *J. Chem. Phys.*, **21**, 1927 (1953).

10) Y. Morino and K. Kuchitsu, *X-ray* (*X sen*), **8**, 37 (1954).

11) The calculation by use of punched cards was carried out by Mr. K. Kuchitsu and Mr. E. Hirota of the University of Tokyo.

calculated values of the mean amplitudes listed in Tables II and III were those calculated by Morino et al.[9] from spectroscopic data, values for the non-bonded F···Cl and the *trans* F···Cl distances were appropriately taken from other data. The values for the *gauche* F···F and the *gauche* Cl···Cl distances were taken from Karle's experimental data on C_2F_6[12] and C_2Cl_6[13] by ascribing the contribution of torsional oscillation to the over-all vibration. For the *gauche* F···Cl distance, an appropriate value was also assumed using Karle's data.

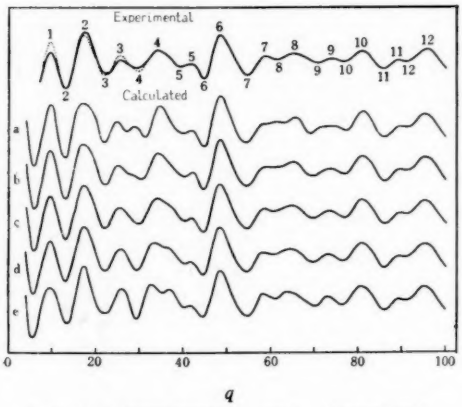

Fig. 4. Experimental and theoretical intensity curves for CF_2Cl-CF_2Cl. In the experimental curve, the dotted line indicates the correction for non-nuclear scatterings. Curves a and e indicate the theoretical intensity curves for the *trans* and the *gauche* form, respectively. Curves b, c and d indicate those for the amount of the *gauche* form of 30, 50 and 70%.

Theoretical intensity curves were computed for the *trans* and the *gauche* form using the values obtained from the RD curve (C—F=1.33$_0$, C—Cl=1.74$_5$, C—C=1.54, ∠CCCl=112°, ∠FCCl=110°, ∠CCF=108° and the azimuthal angle of the *gauche* form=63°) on the assumption that the structural frame of the molecule does not change with rotation about the C—C bond. The curves a and e in Fig. 4 refer to the *trans* and the *gauche* form, respectively. These curves completely disagree with the experimental curve with respect to the features in the region $20<q<40$. The curves b, c and d represent isomeric mixtures, in which the amount of the *gauche* from is 30, 50 and 70 per cent., respectively. The fact that the curve c is in satisfactory agreement with experiments definitely confirms the amount of the *gauche* form estimated above from the RD curve.

In order to determine the range of inaccuracy in various structure parameters, a number of intensity curves were computed for various assumed models which have a C—F distance ranging from 1.31 to 1.38 Å, a C—C distance from 1.46 to 1.58 Å, a C—Cl distance from 1.70 to 1.79 Å, ∠CCF from 106°30′ to 111°, ∠CCCl from 109°30′ to 115°, and ∠ClCF from 104°30′ to 114°30′. Moreover, the azimuthal angle and the amount of the *gauche* form were varied for each assumed model.

In order to determine the limit of one structural parameter, it is desirable to

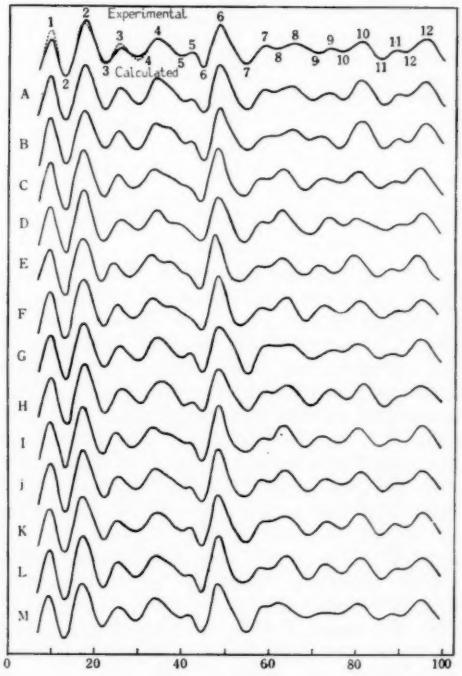

Fig. 5. Experimental and theoretical intensity curves for CF_2Cl-CF_2Cl. In the experimental curve, the dotted line indicates the correction for non-nuclear scattering. The molecular parameters used in the calculation are listed in Table IV.

12) D. A. Swick, I. L. Karle and J. Karle, *J. Chem. Phys.*, **22**, 1242 (1954).
13) D. A. Swick and I. L. Karle, ibid., **23**, 1499 (1955).

TABLE III

THE RESULT OF ANALYSIS OF THE RD CURVE (THE REGION OF NON-BONDED DISTANCE)

		trans form							
		F···F	C···F	F···Cl	C···Cl	$(F\cdots F)_g$	$(F\cdots Cl)_g$	$(F\cdots F)_t$	$(Cl\cdots Cl)_t$
Distance	obs.	2.15	3.33	2.53	2.72	2.72	2.97	3.48	4.29
	calc.	2.16	2.33	2.53	2.73	2.70	2.98	3.46	4.31
Mean amplitude	obs.	—	—	—	—	—	—	—	0.088
	calc.	0.056	0.059	0.065	0.073	0.114	0.120	0.061	0.074

		gauche form					
		$(F\cdots F)_g$	$(F\cdots F)_g$	$(F\cdots Cl)_g$	$(Cl\cdots Cl)_g$	$(F\cdots F)_t$	$(F\cdots Cl)_t$
Distance	obs.	2.62	2.72	2.97	3.30	3.48	3.90
	calc.	2.63	2.71	2.98	3.31	3.46	3.88
Mean amplitude	obs.	—	—	—	—	—	0.062
	calc.	0.114	0.114	0.120	0.125	0.061	0.074

TABLE IV

MOLECULAR PARAMETERS USED IN CALCULATING THE THEORETICAL INTENSITY CURVES SHOWN IN FIG. 5

Model	C—F	C—C	C—Cl	∠CCCl	∠CCF	∠FCCl
A (RD)	1.33_0Å	1.54Å	1.74_5Å	112°	108°	110°
B	1.31	1.54	1.75	112	108	110.5
C	1.35	1.54	1.75	112	108	110.5
D	1.35	1.54	1.73	112	108	110.5
E	1.35	1.54	1.77	112	108	110.5
F	1.34	1.48	1.74	112	108	110.5
G	1.34	1.58	1.74	112	108	110.5
H	1.34	1.54	1.74	112	108	109
I	1.34	1.54	1.74	112	108	111.5
J	1.34	1.54	1.74	111	108	110.5
K	1.34	1.54	1.74	113	108	110.5
L	1.34	1.54	1.74	112	107	110.5
M	1.34	1.54	1.74	112	109	110.5

select the regions in which the intensity curve is unaffected by other parameters. If such regions were not found and the effects of several parameters overlapped, the contribution from other parameters must be considered properly. Some of the computed curves are reproduced in Fig. 5 in order to illustrate the dependence of relative positions and intensities of maxima and minima upon the parameters. The values of the parameters used are listed in Table IV except the amount of the *gauche* form and the azimuthal angle which are kept constant at 50 per cent. and 63°, respectively.

C—F and C—Cl Parameters. — The position of the 6th maximum and the relative depth of 3rd and 4th minima depend mainly upon the C—F and C—Cl parameters[14]. This relation gives the acceptable region in the parameter chart illustrated in Fig. 6. The full lines refer to the position of the 6th maximum, and the broken lines the relative depth of 3rd and 4th minima. The area enclosed by these border lines is the acceptable domain. The positions of dots indicate the parameters of the models for which intensity curves were computed.

C—C Parameter. — The changes of the intensity curves caused by the variation of the C—C parameter, can be improved by the modification of other parameters, because there is no region in which the intensity curve depends solely upon the C—C parameter. In other words, it means that the contribution from the C—C distance is very small. However, the modification of the C—F or the C—Cl parameter makes the position of the 6th maximum shift out of the limit of the experimental error, because the position of the 6th maximum does not depend upon the C—C parameter. Although the change in the C—C distance is accompanied by the changes in the interatomic distances

14) The intensity relation between 3rd and 4th minima depends also upon the abundance ratio of the isomers but the changes are not serious in the region of the amount of the *gauche* form from 40 to 60 per cent.

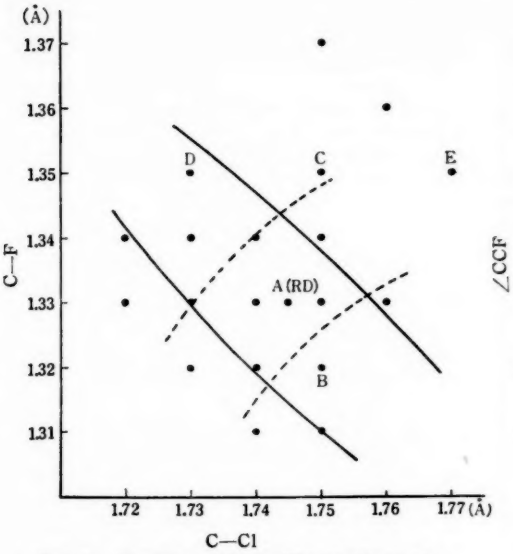

Fig. 6. Parameter chart. The positions of dots indicate the parameters of models for which intensity curves were computed. The positions of letters indicate the parameters of models for which intensity curves are shown in Fig. 5.

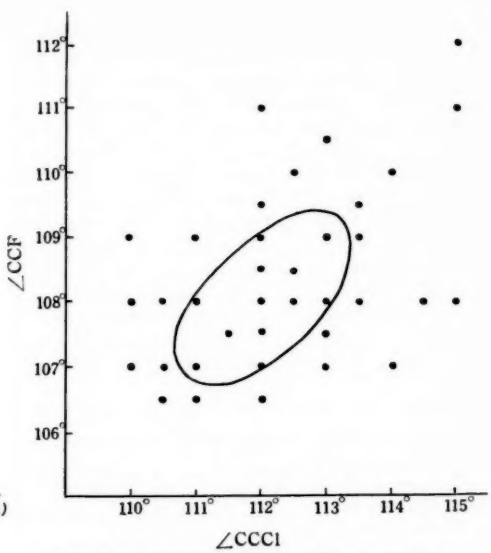

Fig. 7. Parameter chart. The positions of dots indicate the parameters of models for which intensity curves were computed. The area enclosed by the curved line roughly indicates the acceptable region.

TABLE V

COMPARISON BETWEEN EXPERIMENTAL AND THEORETICAL INTENSITY CURVES

Peak		Peak position			Peak height		
min.	max.	q_0	q_c	q_c/q_0	I_0	I_c	I_0/I_c
3		22.0	22.0	1.000	−1.00	−1.12	0.893
	3	25.4	25.4	1.000	+0.42	+0.36	1.167
4		29.5	29.6	1.003	−0.70	−0.82	0.854
	4	33.9	33.9	1.000	+0.86	+1.04	0.827
5		39.5	40.2	1.018	−0.44	−0.56	0.786
	5	41.6	41.8	1.005	−0.29	−0.41	0.707
6		44.5	44.5	1.000	−1.31	−1.42	0.923
	6	48.3	48.3	1.000	+1.87	+2.06	0.908
7		54.7	54.5	0.996	−0.06	−1.11	0.955
	7	58.3	58.3	1.000	+0.46	+0.25	(1.840)
8		61.3	60.6	0.989	+0.05	+0.11	(0.455)
	8	65.0	65.0	1.000	+0.54	+0.50	1.080
9		70.4	69.7	0.990	−0.22	−0.49	(0.449)
	9	74.0	73.5	0.993	+0.11	+0.07	(1.571)
10		76.9	76.7	0.997	−0.13	−0.42	(0.310)
	10	80.8	81.0	1.002	+0.62	+0.94	0.660
11		85.6	86.0	1.005	−0.66	−0.84	0.786
	11	89.1	89.4	1.003	+0.02	−0.05	(——)
12		91.0	91.0	1.000	−0.14	−0.14	(1.000)
	12	95.6	95.4	0.998	+0.78	+0.84	0.929
Average				1.000			0.883
Average deviation				0.003			0.104

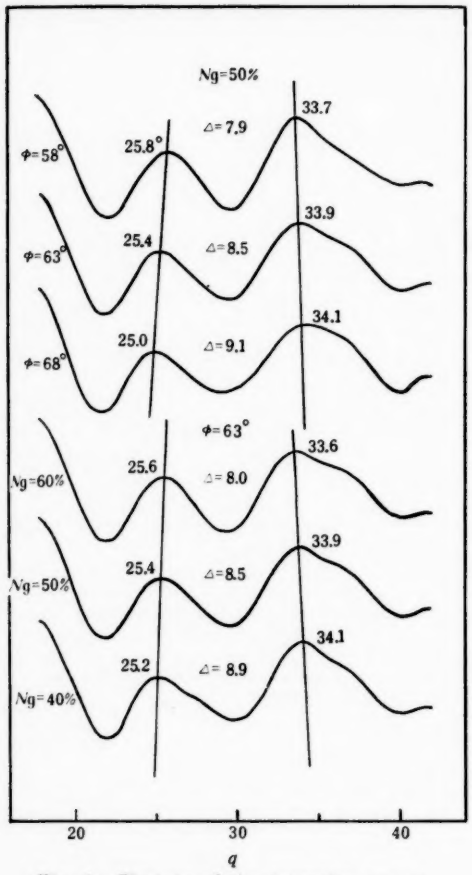

Fig. 8. Changes of the intensity curves with the parameters ϕ and N_g.

between two halves of the molecule, these changes can considerably be compensated by modifying ∠CCF and ∠CCCl parameters. Therefore, the ambiguity of the C—C distance becomes somewhat larger than those of other parameters. The acceptable models could be obtained for the C—C distance ranging from 1.50 to 1.58 Å by means of the suitable combination of other parameters.

∠FCCl Parameter. — This parameter affects sensitively the position of the 9th maximum and the depth of the 6th minimum. The models with ∠FCCl larger than 111° were unacceptable in the position of the 9th maximum, even if various combinations of other parameters, C—Cl or C—C, were considered. The lower limit of ∠FCCl was obtained from the depth of the 6th minimum which depends only upon this parameter. The

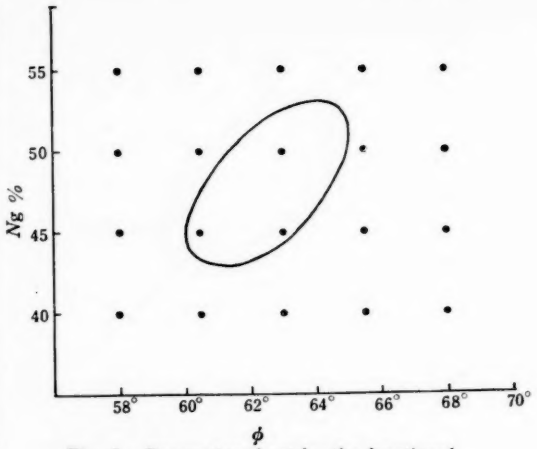

Fig. 9. Parameter chart for the fractional abundance and the azimuthal angle of the *gauche* form. The positions of dots indicate the parameters of models for which intensity curves were computed.

6th minimum is too shallow compared with the experiment for the model with ∠FCCl smaller than 109°. This fault could not be improved by adjusting other parameters.

∠CCF and ∠CCCl Parameters. — As stated above, the effects of ∠CCF and ∠CCCl parameters are compensated by the C—C parameter. Projecting the three dimensional parameter chart composed of the ∠CCF, ∠CCCl and C—C parameters to a ∠CCF—∠CCCl plane, the domain shown in Fig. 7 was obtained as a result of the superposition of a number of domains which are acceptable for various values of the C—C parameter.

The Abundance Ratio and the Azimuthal Angle. — The positions of the 3rd and the 4th maximum depend upon many other parameters, but the interval between these two maxima depends only upon the abundance ratio and the azimuthal angle as shown in Fig. 8. Therefore, this interval can be used to determine the limits of these parameters. Because the positions of the 3rd the 4th maximum can precisely be measured by use of the long camera length, those parameters were determined with considerably little ambiguity, as shown in Fig. 9.

From the analysis described above, the best model and the limits of ambiguity were estimated as follows:

C—F $=1.33_0\pm0.01_5$Å ∠CCF $=108°\pm1°30'$
C—C $=1.54\pm0.04$ Å ∠CCCl $=112°\pm1°30'$.
C—Cl $=1.74_5\pm0.01_5$Å ∠FCCl $=110°\pm1°$

The azimuthal angle of the *gauche* form $=62.5\pm3°$

The amount of the *gauche* form $=48\pm5$ per cent. at 10°C.

For the best model the mean value of $q_{calc.}/q_{obs.}$ and $I_{obs.}/I_{calc.}$ for the maxima and the minima are 1.000 and 0.883 with the average deviation of 0.003 and 0.104, respectively. (See Table V.)

Discussion of the Results

It is interesting to compare the C—F and C—Cl bond distances obtained in this investigation with those on other chlorofluorocompounds having different numbers of fluorine atoms. As shown in Table VI, the C—F distance in a $CF_2Cl—CF_2Cl$ molecule lies between the value of 1.32 Å in $CF_3—CF_3$[12] and that of 1.38 Å in $CFCl_2—CFCl_2$[1]. On the other hand, although the inaccuracy of the data does not permit to draw a definite conclusion, it appears that the C—Cl distance of $CF_2Cl—CF_2Cl$ is shorter than that of C_2Cl_6[15] and $CFCl_2—CFCl_2$[1]. This fact coincides with the results from a number of investigations on the molecular structures of organic fluorine compounds[16] in which the C—F and C—Cl bond distances decrease with the number of the fluorine atoms bonded with the same carbon atom.

TABLE VI

C-F AND C-Cl BOND DISTANCES IN SOME FLUOROCHLOROETHANES

Molecule	C-F (Å)	C-Cl(Å)
CF_3-CF_3	1.32 ± 0.01[12]	
CF_2Cl-CF_2Cl	$1.33_0\pm0.01_5$*	$1.74_5\pm0.01_5$*
$CFCl_2-CFCl_2$	1.38 ± 0.02[1]	1.76 ± 0.01[1]
CCl_3-CCl_3		$\begin{cases}1.77\pm0.02 & [15a)]\\ 1.76_3\pm0.01 & [15b)]\end{cases}$

* Present work.

An abnormal shortening of the C—C bond distance has been reported[17,18] in the early investigations of some organic fluorine compounds as shown in Table VII. However, the recent investigations by Karle[12] and Livingston[19-21] have shown that several fluorine compounds listed in the table have almost normal distances of the C—C bond. Although in the preliminary analysis the abnormally short distance of the C—C bond was assumed, it was found from this more precise analysis that the experimental results could be explained by a normal value of the C—C distance in this molecule. However, because of great inaccuracy of the determination of this distance, a definite conclusion could not be given for the problem of the effect of halogen atoms on the C—C bond distances in organic halides.

TABLE VII

C-C BOND DISTANCES IN SOME FLUOROCARBONS

Molecule	Early results	Recent results
CF_3-CF_3	1.45 ± 0.06[17]	$\begin{cases}1.56\pm0.03 & [12)]\\ 1.51\pm0.06 & [19)]\end{cases}$
CH_3-CF_3	1.45 ± 0.04[17]	$\begin{cases}1.53\pm0.04 & [17)]\\ 1.52\pm0.04 & [20)]\end{cases}$
$CF_3-C_2H_5$	1.49 ± 0.04[18]	
$CF_3-CF_2-CF_3$	1.47 ± 0.03[18]	
CHF_2-CHF_2	1.46 ± 0.05[18]	
$CH_3-CF_2-CH_3$	$\begin{cases}1.51\pm0.02 & [18)]\\ 1.48\pm0.03 & [18)]\end{cases}$	
CF_3-CH_2Cl	1.47 ± 0.03[18]	
CF_3-CCl_3	<1.54[18]	
CF_3CH_2OH		1.52 ± 0.04[21]
CF_2Cl-CF_2Cl		1.54 ± 0.04*

* Present work.

It is to be noted that the value of ∠FCF somewhat smaller than the tetrahedral angle as reported in many organic fluorine compounds except carbon tetrafluoride, seems to be revealed also in this molecule, that is, the value of 108°44′ obtained from other angle parameters is consistent with those in CH_2F_2(108°17′)[22], in CCl_2F_2(109°)[23], and in many other compounds containing a CF_3 group[24].

The problem of the rotational isomerism

15a) Y. Morino and M. Iwasaki, *J. Chem. Phys.*, **17**, 216 (1949).

15b) Y. Morino and E. Hirota, ibid., **28**, 185 (1958).

16) The C—F and the C—Cl distances in many organic fluorine compounds were tabulated in a previous paper. (See ref. 1.)

17) Theae data were quoted from the tabulation compiled by P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).

18) These data were quoted from the tabulation by S. H. Bauer, *U. S. Atomic Energy Com. Report, MDDC* 1494 (1947).

19) J. L. Brandt and R. L. Livingston, *J. Am. Chem. Soc.*, **76**, 2096 (1954).

20) J. L. Brandt and R. L. Livingston, ibid., **78**, 3573 (1956).

21) R. L. Livingston and G. Vanghan, ibid., **78**, 2711 (1956).

22) D. R. Lide, *J. Am. Chem. Soc.*, **74**, 3548 (1952); W. C. Hamilton and K. Hedberg, ibid., **74**, 5529 (1952).

23) L. O. Brockway, *J. Phys. Chem.*, **40**, 747 (1936). According to a recent study by R. L. Livingston and D. H. Lyon (*J. Chem. Phys.*, **24**, 1283 (1956)), the value of 109.5°±3° was obtained. At any rate, because these two values from the visual method of electron diffraction are not free from great uncertainty, more accurate studies by the microwave spectroscopy or the sector—microphotometer method of electron diffraction are desired for the elucidation of the structure of this molecule.

24) Many examples of the data for ∠FCF in the compounds containing a CF_3 group are cited in ref. 20.

in this molecule has previously been studied by several investigators. On the basis of a number of observed Raman lines, Glockler and Sage[25] conculuded that two isomeric forms were present in the liquid state. Simpson and Plyler[26] have studied the infrared spectrum in the vapor state, and carried out a partial assignment on the basis of two isomeric forms. Kagarise[27] has recently studied the dependence of infrared spectra on temperature and state, and concluded that the *trans* isomer persists in the crystalline solid, and is the stable form in the liquid and the vapor state. The energy difference between the isomers in the vapor state was reported to be 500±200 cal./mol.

The energy difference, ΔE, was also obtained from the diffraction data by use of the following formula:

$$\frac{N_g}{N_t} = 2\frac{f_g}{f_t}\exp(-\Delta E/RT) \qquad (6)$$

where f_t and f_g are the vibrational and rotational partition functions of the *trans* and the *gauche* molecules. The factor 2 is introduced to account for the double weight of the *gauche* form. The ratio of f_g to f_t is considered to be approximately equal to unity. Therefore, neglecting the difference between f_g and f_t, the value of 440±110 cal./mol. is obtained from the diffraction data. This result is in good agreement with the value of 500±200 cal./mol. obtained by Kagarise in the vapor state from the temperature dependence of the infrared spectra.

The energy difference for the molecule in question is smaller than the value of 1140 cal./mol.[28] for a $CH_2Cl—CH_2Cl$ molecule in contrast to the fact that methyl substitution[29] does not seriously decrease the energy difference. This lowering of the energy difference is probably caused by the fact that the dipole interaction is not much different between the *trans* and the *gauche* position as a result of the substitution of C—H with C—F, the bond moment of which is almost equal to that of a C—Cl bond. This fact is consistent with the conclusion proposed by Mizushima, Morino and Shimanouchi[30] that the steric repulsion plays an important role in determining the potential barrier but the electrostatic force is the important factor in determining the energy difference between the various configurations. Miyagawa[31] and Kreevoy et al.[32] supported this conclusion by a quantitative calculation.

Summary

The molecular structure of 1,1,2,2-tetrafluoro-1,2-dichloroethane was investigated by means of the sector-microphotometer method of electron diffraction. The existence of two isomeric forms, i.e., *trans* and *gauche*, was confirmed, and the amount of the *gauche* form was found to be 48±5 per cent. at 10°C. This corresponds to the energy difference of 440±110 cal./mol., the *trans* form being more stable than the *gauche* form. The interatomic distances and the bond angles were determined as follows:

C—F $=1.33_0\pm0.01_5$Å $\angle CCF = 108°\pm1°30'$
C—C $=1.54\pm0.04$ Å $\angle CCCl = 112°\pm1°30'$
C—Cl $=1.74_5\pm0.01_5$Å $\angle FCCl = 110°\pm1°$

and the azimuthal angle of the *gauche* form $=62.5°\pm3°$.

The diffraction patterns and the microphotometer records were taken by using apparatuses in Nagoya University. The author wishes to express his sincere gratitude to Professor M. Kubo, Professor R. Uyeda and Dr. M. Kimura for giving him fascility to use the apparatus and for their valuable advice. Thanks are also due to Mr. S. Shibata, Mr. H. Morimoto and Mr. K. Kimura of Nagoya University for their friendly assistance, and to Mr. K. Kuchitsu and Mr. E. Hirota of the University of Tokyo for their help in calculating the theoretical intensity by means of a punched card machine in the Division of Health and Welfare Statistics, Welfare Minister's Secretariat. Further, the author is much indebted to Professor Y. Morino of the University of Tokyo for his helpful criticism of this investigation.

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SHORT COMMUNICATIONS

Solubility of Alcohols in Water Determined by the Surface Tension Measurements

By Kyoji Kinoshita, Hidehiko Ishikawa and Kōzō Shinoda

(Received September 11, 1958)

The solubility data of alcohols in water are very important and useful for the study in colloid chemistry. Surface active molecules, like higher alcohols, aliphatic amines or fatty acids, have an habitual tendency to form supersaturated solution and the solubility determination encounters some difficulties by the use of the usual method[1]. However, the surface tension in aqueous solutions of these substances monotonously decreases up to their saturation concentration and then remains constant in the heterogeneous region. Therefore, it is possible to determine the solubility of surface active substance in water from the surface tension —logarism of concentration curve without the disturbance from supersaturation as it is in some other cases. As the surface tensions change over the common range, namely from 74 to 30 dynes/cm., the accuracy of this method is nearly equal for any alcohol of markedly different solubility. This principle of determining the solubility by surface tension method was proposed already by several authors[2-4]. But, there are few reports expect for those by Addison and Hutchinson[3,6] who determined the solubility of alcohols from the measurement of surface tension by vibrating-jet or vertical plate method.

Experimental. — *n*-Butanol, *n*-pentanol, *n*-hexanol, *n*-octanol, *n*-nonanol and *n*-decanol were purified by vacuum distillation through 50~100cm. column. The boiling points were 11°C, 138°C, 155.7~156°C, 96°C at 16 mmHg, 113~114.5°C at 20 mmHg and 101°C at 5 mmHg, respectively. Heptanol was of Kahlbaum pure grade material. Pentanol and nonanol were synthesized from *n*-propanol and nonanoic acid, respectively. Surface tension was measured by the drop weight method, using a tip of 6 mm. in diameter. The measurements were carried out in a water thermostat at 25±0.05°C. From the surface tension—logarism of concentration curves the saturation points are determined as the intersections of the curves with the horizontal straight lines passing through the lowest experimental points[7]. The experimental error by this method is about 4% or less.

Results and Discussion. — The results are summarized in Table I and plotted in Fig. 1.

TABLE I
THE SOLUBILITY OF ALCOHOLS IN WATER DETERMINED BY SURFACE TENSION MEASUREMENT AT 25°C

Substance	moles/l.	weight %	weight %
Butanol	0.97	7.4	7.35[5] 7.3[9]
Pentanol	0.25	2.2	2.2[9]
Hexanol	0.059	0.60	0.62[9]
Heptanol	0.0146	0.17	0.18[9]
Octanol	0.0038	0.049	0.059[9]
Nonanol	0.00097	0.014	—
Decanol	0.000234	0.0037	0.0037[6]*

* Solubility measured at 20°C.

The logarithms of the solubility of *n*-aliphatic alcohols in water as a function of hydrocarbon chain length showed a linear relationship and is expressed as follows,

$$\log C = -1.39m + 5.53 \qquad (1)$$

Here C is the solubility of alcohol in mole per liter and m the number of carbon atoms in the alcohol molecule studied.

We have, however, no reliable data of the temperature dependence of the solubility of alcohols in water. We may estimate the heat term, at least, the difference of heat of solution due to the change in

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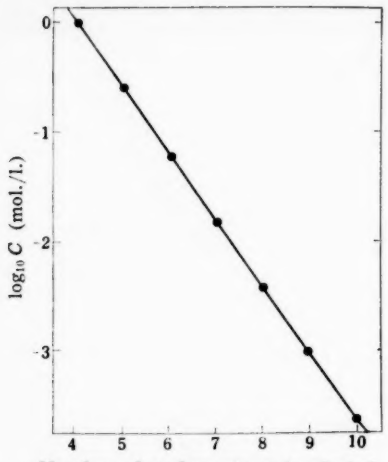

Fig. 1. The relation between the logarithum of the solubility (mole/l.) and the number of carbon atoms in alcohol.

hydrocarbon chain length, by the aid of the following equation[10],

$$0 \cong \ln a_2 = \ln X_2 + \phi_1^2(m\omega + c_2)/kT \qquad (2)$$

Where a_2 is the activity of solute, X_2 the solubility of solute expressed in mole fraction, ϕ_1 the volume fraction of solvent, ω the heat of solution (or the energy) required for passing one methylene group from hydrocarbon medium into water, c_2 the experimental constant, k the Boltzmann constant and T the absolute temperature.

Replacing the solubility values of alcohols in equation 2, we obtain, as the heat of solution, $4.8\,kT$ for R_4OH, $5.6\,kT$ for R_5OH, $6.9\,kT$ for R_6OH, $8.2\,kT$ for R_7OH, $9.6\,kT$ for R_8OH, $11.0\,kT$ for R_9OH and $12.4\,kT$ for $R_{10}OH$. From the difference of these values, the heat (or the energy if there is no volume change) required for passing one methylene group from hydrocarbon medium into water was calculated to be about 811 cal./mole ($1.37\,kT$). (This value is of course very close to the values 823 cal./mole obtained from the slope in Fig. 1, neglecting the change in volume fraction of solute.) This value shows excellent agreement with the value 824 cal./mole obtained by Sasaki and his collaborator[11] for the energy required passing one methylene group from paraffin surface into water.

In connection with this, we draw further attention to the fact that the energy obtained passing one methylene group from water to air-water interface was also determined as 656 cal./mole by the same authors[11]. This value again shows excellent agreement with the value 652~640 cal./mole obtained by Davies[12] and one of us[13,14].

We wish to thank Mr. T. Masumizu for his exploratory work and the Department of Education for the Scientific Research Expenditure.

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*On Lucaconine**

By Takashi Amiya ane Takeo Shima

(Received Septemper 11, 1958)

An alkaloid, lucaconine (I) ($C_{24}H_{39}O_7N$), was first isolated from the roots of *Aconitum luciduculum*, Nakai by Suginome et al.[1,2] in this Laboratory. Moreover, Furusawa[3] has studied the degradation reactions of compound I. The present authors have further investigated the degradation reactions.

Oxidation of compound I with chromium trioxide-pyridine complex yielded neutral products, oxolucaconine (II)[3] ($C_{24}H_{37}O_8N$. $1^3/_4H_2O$), oxolucaconinone-II (III), m. p. 218°, λ_{max} 298 mμ, log ε 1.9 (*Anal.* Found: C, 62.31; H, 7.64; OCH_3, 18.22. Calcd. for $C_{24}H_{35}O_8N$: C, 61.92; H, 7.58; OCH_3, 19.99%) and oxolucaconinedione (IV)[3] ($C_{24}H_{33}O_8N$). Compound III showed a lactam carbonyl band at 6.15 μ and a six-membered ketone carbonyl band at 5.83 μ in the infrared spectrum**.

* Read before the 9th Annual Meeting of the Chemical Society of Japan held in Kyoto, April, 1956 and the Meeting of the Hokkaido Branch of the Chemical Society of Japan held in Muroran, July, 1958. This constitutes a part of a series entitled "The Aconite Alkaloids" by H. Suginome.

1) H. Suginome, S. Kakimoto, J. Sonoda and S. Noguchi, *Rroc. Japan Acad.*, **22**, 122 (1946).
2) H. Suginome and S. Furusawa, in preparation.
3) S. Furusawa, in preparation.

** All infrared spectra were measured in nujol mulls.

To the previously obtained experimental results[3] and the observations so far recorded, the partial formula of I may be extended as follows:

$C_{15}H_{19}$ $(OCH_3)_3$, $(>COH)_2$, $>CHOH$ (five-membered ring), $>CHOH$ (six-membered ring), $>NC_2H_5$

Lucaconine.

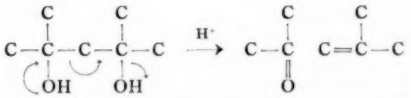
Next, oxidation of a naturally occurring base, monoacetyllucaconine (V)[2] ($C_{26}H_{41}O_8N$), with chromium trioxide-pyridine complex, followed by hydrolysis, afforded compound III. This fact shows that an acetylated hydroxyl group in compound V is the secondary one attached to a carbon atom in a five-membered ring.

It was reported that on treatment of each of compound I or its derivatives, except compound IV, with acetyl chloride, one molecule of water was lost and an anhydro-compound was produced[3].

Anhydrodiacetyllucaconine (VI)[3] ($C_{28}H_{41}O_8N$), obtained by the treatment of lucaconine (I) with acetyl chloride, showed carbonyl bands at 5.77 and 5.81 μ due to ester carbonyl groups and a ketone carbonyl group newly formed by dehydration, but no hydroxyl band in the infrared spectrum.

On hydrogenation over platinum in acetic acid, compound VI absorbed one mole of hydrogen and yielded anhydrodihydrodiacetyllucaconine (VII), m. p. 175° (*Anal.* Found: C, 64.42; H, 8.03; OCH_3, 17.54. Calcd. for $C_{28}H_{43}O_8N$: C, 64.47; H, 8.31; OCH_3, 17.85%), showing carbonyl bands at 5.77 and 5.93 μ due to the ester carbonyl groups and the ketone carbonyl group; no hydroxyl band appeared in the infrared spectrum. On hydrolysis, compound VII splits off two moles of acetic acid to give anhyrodihydrolucaconine (VIII), m.p. 210° (*Anal.* Found: C, 65.98; H, 9.11. Calcd, for $C_{24}H_{39}O_6N$: C, 65.87; H, 8.98%). The infrared spectrum of compound VIII showed a band at 5.92 μ characteristic of a ketone carbonyl group. On reduction of compound VIII by lithium aluminum hydride, followed by acetylation with acetic anhydride in pyridine, anhydrodihydrotriacetyllucaconinol (IX) yielded, m. p. 130~133° (*Anal.* Found: C, 64.19; H, 8.62; OCH_3, 19.66; $COCH_3$, 20.18. Calcd. for $C_{30}H_{47}O_9N$: C, 63.69; H, 8.38; OCH_3, 18.23; $COCH_3$, 22.83%) showing neither keton carbonyl band near 5.92 μ nor hydroxyl band in the infrared spectrum. On reduction of compound VI with lithium aluminum hydride, anhydrolucaconinol (X), m.p. 185~190° (*Anal.* Found: C, 66.22; H, 8.74; OCH_3, 20.31. Calcd. for $C_{24}H_{39}O_6N$: C, 65.87; H, 8.98; OCH_3, 21.25%) was given, showing no ketone carbonyl band in the infrared spectrum. On treatment of compound III with acetyl chloride, followed by hydrolysis and further oxidation by chromium trioxide-pyridine complex, anhydrooxolucaconinedione (XI) ($C_{24}H_{31}O_7N$) was produced. This had previously been obtained from VI through two steps[3].

These experiments indicate that in each compound, VI and XI, obtained by treatment with acetyl chloride both a ketone carbonyl group and a double bond were formed with elimination of one mole of water, and, moreover, that this dehydration took place between the two tertiary hydroxyl groups. This dehydration reaction seems to be one of 1—3 cleavages[4] and the following mechanism may be shown.



Wolf-Kishner reduction of lucaconinone-I (XII) ($C_{24}H_{37}O_7N$), which was previously prepared[3] and showed a five-membered ketone carbonyl band at 5.72 μ, gave deoxylucaconinone-I (XIII), m. p. 165° (*Anal.* Found: C, 66.16; H, 8.96; OCH_3, 19.25. Calcd. for $C_{24}H_{39}O_6N$: C, 65.87; H, 8.98; OCH_3, 21.27%), showing no band characteristic of the ketone carbonyl group in the infrared spectrum. Treatment of compound XIII with acetyl chloride, followed by hydrogenation over platinum in acetic acid, gave anhydrodihydromonoacetyldeoxylucaconinone-I (XIV), m. p. 84~90° (*Anal.* Found: C, 67.41; H, 9.26; OCH_3, 21.58; $COCH_3$, 10.36. Calcd. for $C_{26}H_{41}O_6N$: C, 67.36; H, 8.91; OCH_3, 20.08; $COCH_3$, 9.28%), showing carbonyl bands at 5.79 and 5.93 μ due to an ester carbonyl and a ketone carbonyl group formed by dehydration but no hydroxyl band in the infrared spectrum.

On the other hand, it was previously shown that treatment of compound I with acetyl chloride gave the anhydro-compound VI with loss of a mole of water, and that, on the contrary, the same treatment of compound IV, gave monoacetyloxolucaconinedione (XV) [$C_{24}H_{32}O_8N(COCH_3)$] without elimination of water[3].

On the basis of the above-mentioned experimental results, it may be shown that whilst on treatment of each of compounds I, III and XIII, which contained no five-membered ketone carbonyl group, with acetyl chloride, a mole of water was lost, on the same treatment of compound IV water was not lost. Accordingly, it may be reasonably concluded that dehydration by acetyl chloride occurs in such a case that a secondary hydroxyl group attached to the carbon atom in the five-membered ring is present or substituted for hydrogen atom, and that dehydration does not occur on

4) S. Archer, T. R. Lewis and B. Zenitz, *J. Am. Chem. Soc.*, **80**, 958 (1958).

the contrary in such a case that the above hydroxyl group is converted into a ketone carbonyl group.

The authors are grateful to Professor Harusada Suginome, President of Hokkaido University, for his unfailing kindness in encouraging this work, and to Messrs. M. Yamaguchi and A. Fujino, Institute of Polytechnics, Osaka City University, for their kindness in the determination of the infrared spectra.

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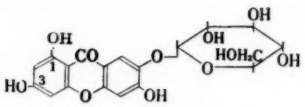
Additions and Corrections

Volume 30, 1957

S. Iseda: On Mangiferin, the Coloring Matter of Mango (Mangifera indica Linn.). V.
Page 631. Formulae II should read



T. Tokuda: Crystallization of Quartz at High Temperatures.
Page 692. In col. 1, line 16, for "cm" read "cm^2".

Additions and Corrections

Volume 31, 1958

S. Ono, T. Kuge and N. Koizumi: Dielectric Properties of Starch. II.
Page 42. In legend to Fig. 5, for "at the inscribed amounts (g./100 g. dry starch)." read ", where each straight line corresponds, from left to right, to its amount 0.00(v), 0.00, 0.00, 1.05, 1.16, 1.62, 3.35, 6.24, 8.84, 8.37, 9.80, 13.3 and 17.5 (g./100 g. dry starch), respectively.".

K. Narita, S. Fujiwara and S. Murasawa: A Method for the Fractionation of Oligopeptides Based on their Molecular Sizes.
Page 383. In Table II, for "0.3% HCl**" read "0.3% HCl***".
Page 385. In col. 2, the first line, for "DL-alanylglycine" read "DL-alanylglycylglycine".
Page 387. In col. 2, line 12, for "othe" read "other".

T. Suga: The Synthesis of Carvone from α-Terpinyl Acetate.
Page 570. In Table I, in col. 2, for "I : 5" read "1 : 5", in col. 5, for "I5" read "15".
Page 571. In col. 2, line 26, for "(acetic acid)," read "acetic acid".
Page 573. In col. 1, in foot-note, line 3 from bottom, for "152~153°" read "152~153°C".
In col. 2, line 3, for "8-Hydroxycarvotanacetone. (IIa)" read "8-Hydroxycarvotanacetone (IIa).".

T. Tokuda: Relations between the Substructure and the Rate of the Sluggish Inversion of Quartz Rock.
Page 742. In Table I, for "Recrystallized part in red-white silica stone" read "Recrystallized red cherty part in red-white silica stone".
Page 743. In Fig. 1, for "Numbers (1—14)" read "Numbers (1—16)".
Page 745. The author's adress should be corrected as "Institute of Scientific and Industrial Research, Osaka University, Sakai, Osaka".

K. Hata, K. Watanabe and M. Tanaka: Vapor Phase Catalytic Hydrogenation of Organic Compounds Using Stabilized Nickel Catalyst.
Page 775. In col. 2, line 10, for "which" read "using".

K. Hata, S. Taira and I. Motoyama: A New Type of Urushibara Nickel Catalyst.
Page 777. In Fig. 1, add "×70" as magnification.

H. Yamatera: On the Absorption Spectra of Hexamminecobalt(III) and Related Complexes. II.
Page 103. Along the abscissa of Fig. 3, for "0.2, 0.4, 0.6, etc." read "0.02, 0.04, 0.06, etc."
Page 103. In col. 2, line 4 from the bottom, for every "3" read "5".
Page 107. In col. 1., line 30, for "unreasonably" read "very".

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(Printed in Japanese)

Vol. 79, No. 4 (April, 1958)

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M. HAYASHI: Vibrational Spectra and Molecular Form of Chloromethyl-dimethyl-chlorosilane and its Related Compound.

Y. MASHIKO: Vibrational Spectrum of Dimethyl Ether.

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N. IZUMIYA et al.: Synthesis of Peptides. II. Synthesis of Dipeptides Involving the Amino Group of L-Tyrosine in Peptide Bond.

T. KUBOTA et al.: Chemical Studies on the Black Rot Disease of Sweet Potatoes. XVI. On the Stereochemical Structure of Ipomeamaron.

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K. SUGA: Sythesis of 1,8-Dibromo-2,6-octadien-4-yne.

H. WATANABE et al.: Molecular Compounds of Berberine Hydrochloride and Sulfanilamides.

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(Printed in Japanese)

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M. SUZUKI et al.: Heat of Vinyl-copolymerization.

S. TAKAHASHI: Studies on the Decompositions of HCN Gas by Electric Discharge. II. On the Decompositions by Silent Discharge.

S. MIYAZAKI et al.: Studies on the Chemical Reaction of High Frequency Electric Discharge. X. Effects of Glass Surfaces on the Formations

of HCN from CH_4-N_2, CH_4-N_2-H_2. XI. Effects of Frequency on the Formations of HCN. XII. Formations of HCN from CH_4-N_2, CH_4-N_2-H_2.

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S. KOBAYASHI: Volumetric Determination of Chlorine in Silicate Rocks.

H. MIURA: On the Origin of the Spring Water from Ôfuki in the Region of the Hot Springs Tamagawa.

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